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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF PREVENTION, PESTICIDE AND TOXIC SUBSTANCES

OPP OFFICIAL RECORD
HEALTH EFFECTS DIVISION
SCIENTIFIC DATA REVIEWS
EPA SERIES 361

MEMORANDUM

Date: 10/29/09

SUBJECT: **Pyraclostrobin.** Petition for New Uses and Tolerances on Alfalfa. Summary of Analytical Chemistry and Residue Data.

PC Code: 099100
Decision No.: 405748
Petition No.: 9F7528
Risk Assessment Type: NA
TXR No.: NA
MRID No.: 47584401

DP Num.: D367409
Registration No.: 7969-186, 7969-266, and 7969-199
Regulatory Action: Section 3 Registration
Case No.: NA
CAS No.: 175013-18-0
40 CFR: 180.582

Ver.Apr.08

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RD (7509P)

This document was originally prepared under contract by Dynamac Corporation and revised to reflect current Office of Pesticide Programs (OPP) policies.

Executive Summary

Pyraclostrobin, methyl [2-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl]phenyl] methoxycarbamate, belongs to the strobilurin class of fungicides, which are synthetic analogs of a natural antifungal substance that inhibits spore germination, mycelial growth, and sporulation of the fungi on the leaf surface. Pyraclostrobin is currently registered to BASF Corporation (BASF) for use on a wide variety of field, vegetable, fruit, and nut crops for direct foliar applications and on field and vegetable crops as a seed treatment. It is formulated as water-dispersible granules (WDG), emulsifiable concentrates (EC), or suspension concentrates (SC =

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FIC). For field uses, pyraclostrobin is typically applied as foliar applications using ground or aerial equipment at maximum seasonal rates of 0.3-3.0 lb ai/A.

Pyraclostrobin tolerances for plant commodities are listed in 40 CFR §180.582 (a)(1) and are expressed in terms of the combined residues of the pyraclostrobin and its desmethoxy metabolite BF 500-3 (methyl N-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl carbamate), expressed as parent compound. The established tolerances for plant commodities range from 0.02 ppm in/on wheat grain to 30 ppm in/on cotton gin byproducts. Tolerances for pyraclostrobin in livestock commodities are listed in 40 CFR §180.582 (a)(2) and are expressed in terms of the combined residues of the pyraclostrobin and its metabolites convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol (BF 500-5) and 1-(4-chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol (BF 500-8), expressed as parent compound. The established tolerances for livestock commodities range from 0.1 to 1.5 ppm; no tolerances are established for poultry commodities.

BASF is proposing new uses for pyraclostrobin on alfalfa as a seed treatment and as broadcast foliar applications. A 1.67 lb/gal EC formulation (Stamina™ Seed Treatment Fungicide; EPA Reg. No. 7969-266) is proposed for use as a seed treatment on alfalfa at a rate of 0.02-0.04 lb ai/100 lb seed. Another 2.09 lb/gal EC formulation (Headline® Fungicide; EPA Reg. No. 7969-186) is proposed for up to three broadcast foliar applications to alfalfa under conditions favorable to disease development at rates of 0.098-0.147 lb ai/A and retreatment intervals (RTIs) of 14-21 days. The maximum seasonal use rate is 0.44 lb ai/A, and no more than 2 applications may be applied per cutting. The field applications can be made using ground or aerial equipment, and the proposed preharvest interval (PHI) is 14 days for alfalfa. ARIA notes that BASF has also requested registration of a WDG formulation (Pristine® Fungicide; EPA Reg. No. 7969-199) containing 12.8% pyraclostrobin and 25.2% boscalid for field use on alfalfa under a separate petition (PP#9F7527). The proposed use directions for alfalfa for this WDG multiple active ingredient (MAI) formulation are essentially identical to the 2.09 lb/gal EC formulation. In conjunction with these uses, BASF is proposing permanent tolerances for the combined residues of pyraclostrobin and its metabolite BF 500-3, expressed as parent, on the following commodities:

Alfalfa, forage	9 ppm
Alfalfa, hay	27 ppm

The nature of pyraclostrobin residues in primary crops and livestock are adequately understood, based on the acceptable metabolism studies on grapes, potatoes, wheat, goats and hens. For purposes of the tolerance expression and dietary risk assessment, the HED Metabolism Assessment Review Committee (MARC) has concluded that the residues of concern in plant commodities include pyraclostrobin and its desmethoxy metabolite (BF 500-3), and the residues of concern in livestock commodities include pyraclostrobin and its metabolites convertible to BF 500-5 and BF 500-8.

Adequate analytical methods are available for enforcing pyraclostrobin tolerances and collecting data on residues in plant commodities. The analytical methods, liquid chromatography with tandem mass spectrometric detection (LC/MS/MS) and high pressure liquid chromatography with ultra-violet detector (HPLC/UV), for plant commodities determine pyraclostrobin and its desmethoxy metabolite (BF 500-3). Residues in plant commodities from the current field trials

were determined using a LC/MS/MS data collection method (BASF Method D9908). This method was adequately validated in conjunction with the field trial analyses, and the validated limit of quantitation (LOQ) was 0.02 ppm for pyraclostrobin and metabolite BF 500-3 in alfalfa, for a combined LOQ of 0.04 ppm

Adequate methods are also available for enforcement of the current livestock tolerances. An LC/MS/MS method (BASF Method 446/1) is available for determining residues of pyraclostrobin and its metabolites convertible to BF 500-5 and BF 500-8, expressed in parent equivalents. The validated method LOQ for combined BF 500-5 and BF 500-8 residues, in parent equivalents, is 0.02 ppm for milk and 0.10 ppm for tissues. This method has undergone a successful independent laboratory validation (ILV) trial and a radiovalidation trial. A similar LC/MS/MS method (BASF Method D9902) is available for determining residues of pyraclostrobin and its metabolites convertible to BF 500-5 and BF 500-9, expressed in parent equivalents. The validated method LOQ for combined BF 500-5 and BF 500-9 residues, in parent equivalents, is 0.1 ppm in eggs and poultry tissues. Given the similarity in extraction and purification procedures between Methods 446/1 and D9902, radiovalidation data are not required for Method D9902. However, an acceptable ILV trial and tolerance method validation (TMV) is required for Method D9902 before it can be approved for tolerance enforcement.

Analytical reference standards for pyraclostrobin and its regulated plant metabolite (BF 500-3) are available at the EPA National Pesticide Standards Repository. However, reference standards are not available for the common moieties (BF 500-5, BF 500-8, and BF 500-9) determined by the livestock analytical methods.

The available field trial data adequately support the proposed use of the WDG formulation of pyraclostrobin on alfalfa. An adequate number of tests were conducted using the WDG formulation in the appropriate geographic regions at ~1x the maximum proposed rate, and the appropriate samples were collected from each test around the proposed PHI. Samples were analyzed using adequate methodology and the field trial data are supported by the available storage stability data. Although no alfalfa field trials were conducted using the proposed EC formulation, previously submitted side-by-side field trials on tomatoes, cucumbers, and grapes comparing WDG and EC formulations have shown that residues resulting from the two types of formulations are similar. Therefore, the available data for the WDG formulation will also cover the use of the EC formulations on alfalfa. The available data support tolerances of 10 ppm for alfalfa forage and 30 ppm for alfalfa hay. A revised Section F is required.

No field trial data were submitted reflecting the proposed seed treatment use on alfalfa, but none is required as the seed treatment rate (0.008 lb ai/A) is negligible compared to the proposed foliar applications.

Adequate cattle and poultry feeding studies are available. Based on the dietary burdens and the data from the cattle feeding study, the current tolerances for milk and cattle, goat, horse, sheep, and hog commodities are adequate. Based on the dietary burden and data from the poultry feeding and metabolism studies, tolerances at the method LOQ (0.1 ppm) should be established for poultry meat, fat and meat byproducts, and eggs. A revised Section F is required. The establishment of the new tolerances should be a condition of the registration of the alfalfa use

pending the receipt and acceptance of the ILV and TMV of the proposed poultry enforcement method.

Adequate confined and limited rotational crop studies are available that support the 14-day plant-back interval (PBI) specified on the labels for rotated crops without primary uses of pyraclostrobin. The current rotational crop restrictions are adequate for the proposed use on alfalfa.

Regulatory Recommendations and Residue Chemistry Deficiencies

Several deficiencies related to enforcement methods and analytical standards must be resolved as a condition of registration (see below). Pending resolution of the residue chemistry deficiencies, ARIA recommends for establishing new pyraclostrobin tolerances at 10 ppm on alfalfa forage and 30 ppm on alfalfa hay. The existing tolerances for milk, fat, meat, liver and meat byproducts of cattle, goats, horses, sheep, and hogs will adequately cover the use of pyraclostrobin on alfalfa. However, new tolerances are required on several poultry commodities (see below). A human health risk assessment for pyraclostrobin is forthcoming.

- The proposed LC/MS/MS tolerance enforcement method for poultry commodities (BASF Method D9902) must undergo an acceptable ILV and TMV prior to being approved as an enforcement method.

- Analytical standards for BF 500-5, BF 500-8 and BF 500-9, which are the common moiety analytes determined by the livestock commodity enforcement methods, must be submitted to the EPA National Pesticide Standards Repository.

- A revised Section F for the residues of pyraclostrobin on alfalfa forage at 10 ppm and alfalfa hay at 30 ppm is required.

- Based on the calculated dietary burden for poultry and data from the poultry feeding and metabolism studies, tolerances should be established for poultry meat, fat and meat byproducts, and eggs each at 0.1 ppm. A revised Section F is required. Poultry tolerances for poultry commodities should be established under 180.582(a)(3), and the tolerance expression should read as follows:

  "Tolerances are established for the combined residues of the fungicide pyraclostrobin carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester and its metabolites convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol and 1-(3-chloro-4-hydroxyphenyl)-1H-pyrazol-3-ol, expressed as parent compound, in or on the following raw agricultural commodities."

It is further recommended that the tolerance expressions [40 CFR § 180.474(a)(1) and 40 CFR §180.474 (a)(2) and 40 CFR § 280.474 (c)] be amended to reflect the new *Interim Guidance on Tolerance Expressions* (S. Knizner, 05/27/09). The existing language for 40 CFR § 180.582(a)(1) is:

(a) General. (1) Tolerances are established for combined residues of the fungicide expressed as parent compound, in or on the following raw agricultural commodities.

The above quoted phrase should be replaced with the following:

(a) General. (1) Tolerances are established for residues of the fungicide pyraclostrobin, including its metabolites and degradates, in or on the commodities in the table below. Compliance with the tolerance levels specified below is to be determined by measuring only the sum of pyraclostrobin (carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester) and its desmethoxy metabolite (methyl-N-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenylcarbamate), calculated as the stoichiometric equivalent of pyraclostrobin, in or on the commodity.

The existing language for 40 CFR § 180.582(a)(2) is

(2) Tolerances are established for combined residues of the fungicide pyraclostrobin carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester and its metabolites convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol and 1-(4-chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol, expressed as parent compound, in or on the following raw agricultural commodities.

The above quoted phrase should be replaced with the following:

(2) Tolerances are established for residues of the fungicide pyraclostrobin, including its metabolites and degradates, in or on the commodities in the table below. Compliance with the tolerance levels specified below is to be determined by measuring only those pyraclostrobin (carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester) residues convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol and 1-(4-chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol, expressed as the stoichiometric equivalent of pyraclostrobin, in or on the commodity.

The existing language for 40 CFR § 180.582(b) is

(b) Section 18 emergency exemptions. A time-limited tolerance is established for combined residues of the fungicide pyraclostrobin, (carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl] phenyl]methoxy-, methyl ester) and its desmethoxy metabolite (methyl-N-[[[1-(4-chlorophenyl) pyrazol-3-yl]oxy]o-tolyl]carbamate) in connection with use of the pesticide under section 18 emergency exemptions granted by EPA. The time-limited tolerance will expire and is revoked on the date specified in the following table.

The above quoted phrase should be replaced with the following:

(b) Section 18 emergency exemptions. A time-limited tolerance is established for residues of the fungicide pyraclostrobin, including its metabolites and degradates, in or on the commodities in the table below. Compliance with the tolerance levels specified below is to be determined by measuring only those pyraclostrobin (carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester) residues convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol and 1-(4-chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol, expressed as the stoichiometric

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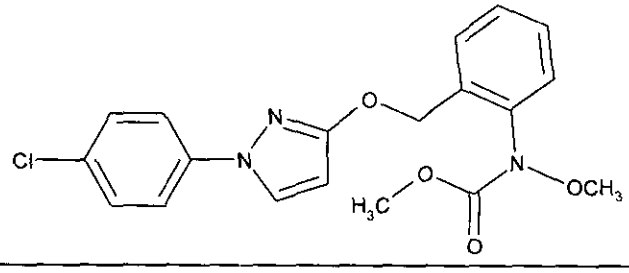
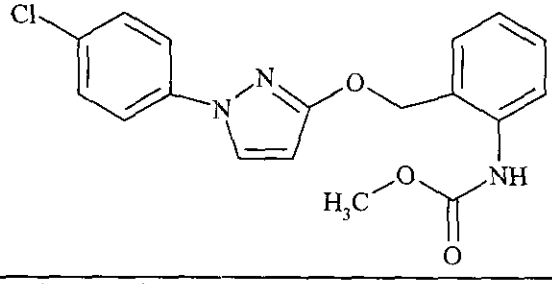
equivalent of pyraclostrobin, in or on the commodity in connection with use of the pesticide under section 18 emergency exemptions granted by EPA. The time-limited tolerance will expire and is revoked on the date specified in the following table.

Note to PM: The tolerance for horse liver was established at 0.1 ppm in 40CFR 180.582(a)(2). However, the tolerance was established in error. The body of the FR Notice indicates that the tolerance was intended to be 1.5 ppm while the final table lists 0.1 ppm ([FR Doc. 02-24487, Filed 9/26/02). This should be corrected.

Background

Pyraclostrobin belongs to the strobilurin class of fungicides, which are synthetic analogs of a natural antifungal substance which inhibits spore germination and inhibits mycelial growth and sporulation of the fungus on the leaf surface. Pyraclostrobin, formulated as an EC, WDG or SC, is currently registered to BASF for seed treatment uses on field and vegetable crops and for foliar application(s) to a variety of field, vegetable, fruit, and nut crops. In the current petition (PP#9F7528), BASF is proposing a new uses for pyraclostrobin on alfalfa as a seed treatment and/or for foliar applications. The nomenclature for pyraclostrobin and its regulated plant metabolite is summarized in Table 1, and the physicochemical properties of technical grade pyraclostrobin are summarized in Table 2.

TABLE 1. Nomenclature of Pyraclostrobin and its Desmethoxy Metabolite.

Compound	
Common name	Pyraclostrobin
Company experimental name	BAS 500 F
Molecule weight	387.8
IUPAC name	methyl *N*-{2-[1-(4-chlorophenyl)-1*H*-pyrazol-3-yloxymethyl]phenyl}(*N*-methoxy) carbamate
CAS name	methyl [2-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS registry number	175013-18-0
End-use product (EPs)	12.8% WDG (Pristine® Fungicide; EPA Reg. No. 7969-199; also contains 25.2% boscalid) 1.67 lb/gal EC (Stamina™ Fungicide Seed Treatment; EPA Reg. No. 7969-266) 2.09 lb/gal EC (Headline® Fungicide; EPA Reg. No. 7969-186)
Regulated plant metabolite	
Common name	pyraclostrobin desmethoxy metabolite
Company experimental name	BF 500-3
Molecular weight	357.8

There are currently 12 end-use products (EPs) containing pyraclostrobin that are registered to BASF in the U.S. for use on food/feed crops. Five of these EPs are registered for only seed treatment and are formulated as 12.8% or 20% WDGs or 0.83-1.67 lb/gal ECs. The remaining seven EPs are registered for field applications to a variety of food/feed crops and are formulated as 6.7-20% WDGs, 1.08 or 2.09 lb/gal ECs, or 1.22 or 2.08 lb/gal SCs. Of the 12 EPs with food/feed uses, six are MAI formulations.

In this petition, BASF is proposing a new seed treatment use for pyraclostrobin on alfalfa for a 1.67 lb/gal EC formulation (Stamina™ Fungicide Seed Treatment; EPA Reg. No. 7969-266), and a field application use on alfalfa for a 2.09 lb/gal EC formulation (Headline® Fungicide; EPA Reg. No. 7969-186). Example labels containing the proposed use directions were provided for the 1.67 and 2.09 lb/gal EC formulations, and the use directions are summarized below in Table 4. Although not included in the current petition, the proposed use pattern for the 12.8% WDG on alfalfa is also summarized below.

TABLE 4. Summary of Directions for Use of Pyraclostrobin.

Applic. Timing, Type, and Equip.[1]	Formulation [EPA Reg. No.]	Applic. Rate	Max. No. Applic. per Season	Max. Seasonal Applic. Rate (lb ai/A)	PHI (days)	Use Directions and Limitations [2]
Alfalfa (seed treatment)						
Seed treatment using standard slurry or mist-type seed treatment equipment	1.67 lb/gal EC [7969-266]	0.02-0.04 lb ai/100 lb seeds	1	0.008 [3]	NA	Do not use treated seed for food, feed or oil purposes
Alfalfa (field application)						
Broadcast foliar applications when conditions are favorable to disease development; ground or aerial equipment.	2.09 lb/gal EC [7969-186]	0.098-0.147 lb ai/A	3 (2 per cutting)	0.44	14	The minimum RTI is 14 days. For aerial applications, use a minimum of 5 gal/A
	12.8% WDG [4] [7969-199]	0.096-0.144 lb ai/A		0.43	14	

1 Ground application may be made through the following types of irrigation systems: center pivot, lateral move, end tow, side wheel roll, traveler, big gun, solid set, or hand move.

2 Use directions allow for the use of spray adjuvants, and specify a 14-day plant-back interval for rotational crops without registered uses for pyraclostrobin.

3 The maximum field use rate for the seed treatment was calculated assuming a planting rate of 5-20 lb of alfalfa seed/A.

4 This formulation is a MAI containing 12.8% pyraclostrobin and 25.2% boscalid. Use directions were obtained from PP#9F7527.

Conclusions: The submitted use directions are sufficient to allow for evaluation of the submitted residue data relative to the proposed use pattern. The available field trial data, which were conducted using a WDG formulation, will support the proposed field uses of the WDG and EC formulations.

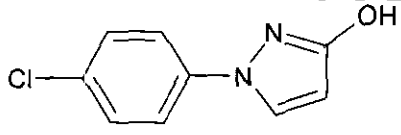
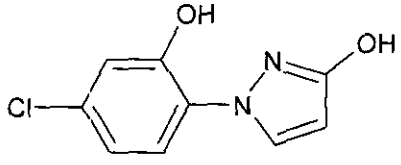
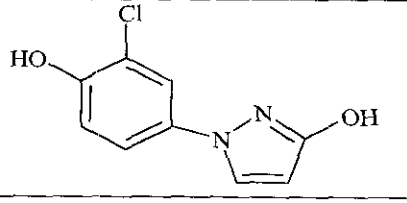
Although no field trial data were submitted reflecting the proposed seed treatment use, no seed treatment residue data are required because the seed treatment rate is negligible compared to the proposed foliar applications. Based on typical seeding rates for alfalfa (2-20 lb seed/A), the maximum seed treatment rate (0.04 lb ai/100 lb seed) would be equivalent to a field use rate of 0.008 lb ai/A, compared to the maximum foliar rate of 0.44 lb ai/A.

860.1300 Nature of the Residue - Plants

TABLE 1. Nomenclature of Pyraclostrobin and its Desmethoxy Metabolite.	
Chemical name	Methyl-N-[[[1-(4-chlorophenyl) pyrazol-3-yl]oxy]o-tolyl] carbamate

TABLE 2. Physicochemical Properties of Technical Grade Pyraclostrobin.					
Parameter	Value				References [1]
Melting point/range	63.7-65.2°C				D269848 & D274191
pH	Not reported				D269848 & D274191
Density	1.285 g/cm^3 at 20°C				D269848 & D274191
Water solubility at 20°C	2.41 mg/L (deionized water) 1.9 mg/L (pH 7) 2.3 mg/L (pH 4) 1.9 mg/L (pH 9)				D269848 & D274191
Solvent solubility (g/100 mL at 20°C)	acetone	16-20	ethyl acetate	6.7-8.0	D269848 & D274191
	methanol	4-5	2-propanol	<0.01	
	acetonitrile	4-5	dichloromethane	20-25	
	toluene	2-5	n-heptane	<0.01	
	1-octanol	<0.01	olive oil	2.9	
	N,N-DMF	>25			
Vapor pressure	2.6 x 10^{-10} hPa at 20°C 6.4 x 10^{-10} hPa at 25°C				D269848 & D274191
Dissociation constant, pK_a	Does not dissociate in water.				D269848 & D274191
Octanol/water partition coefficient, Log(K_{OW}) at room temperature	3.80 at pH 6.2 4.18 at pH 6.5				D269848 & D274191
UV/visible absorption spectrum	λ_{max} = 275 nm				D269848

[1] Product Chemistry data were reviewed by the Registration Division (DP#s 269848 and D274191, 5/3/01, 5/15/01, and 6/7/01, S. Malak).

TABLE 3. Chemical Structures of Pyraclostrobin Metabolites	
Metabolites	Structure
BAS 500-5 1-(4-chlorophenyl)-1H-pyrazol-3-ol	
BAS 500-8 1-(4-chloro-2-hydroxyphenyl)-1H-pyrazol3-3-ol	
BAS 500-9 1-(3-chloro-4-hydroxyphenyl)-1H-pyrazol-3-ol	

860.1200 Directions for Use

radiovalidation data were submitted for both methods and forwarded to ACB/BEAD for a petition method validation. However, following the SOP (ACB-019) for reviewing tolerance methods (September 15, 2008), HED has determined that Method D9904 is suitable as an enforcement method (PP#s 8F7385, 8F7390, and 8E7394; DP Num 343700; B. O'Keefe; 9/7/07).

In the current alfalfa field trials, samples of forage and hay were analyzed for residues of pyraclostrobin and BF 500-3 (expressed as parent) using an LC/MS/MS method (BASF Method D9908). This method is similar to one of the proposed enforcement methods and was first reviewed in conjunction with assorted petitions covering a wide variety of crops (DP# 281042, L. Cheng, 7/26/04).

For this method, residues are extracted from forage and hay with methanol:water:2 N HCl (70:25:5; v/v/v) and centrifuged. Residues are then diluted with 1N HCl, saturated with NaCl, and partitioned into cyclohexane. Residues were concentrated to dryness, re-dissolved in methanol:water:4 mM ammonium formate (80:20:0.1, v/v/v), and analyzed by LC/MS/MS using external calibration curves. Residues were detected and quantified by monitoring the *m/z* 388→194 transition for pyraclostrobin and the *m/z* 358→164 transition for BF 500-3. Residues of BF 500-3 are expressed in parent equivalents. The validated LOQ was 0.02 ppm for each analyte, and the LOD was 0.004 ppm. The LOQ for combined residues is 0.04 ppm. The method was adequately validated in conjunction with the analysis of field trial samples using control samples of alfalfa forage and hay fortified with each analyte at 0.02 and 50.0 ppm.

Animal commodities: Two tolerance enforcement methods have been proposed for ruminant commodities. One is an HPLC/UV method 439/0, which determines residues of pyraclostrobin *per se*, and Method 446, which consists of a gas chromatography with mass spectroscopy detector (GC/MS) Method 446/0 and LC/MS/MS Method 446/1. Method 446 includes a hydrolysis step, and determines residues of pyraclostrobin and its metabolites as BF 500-5 and BF 500-8. The validated method LOQs for BF 500-5 type residues, in parent equivalents, are 0.01 ppm for milk and 0.05 ppm for tissues, and the validated LOQs for BF 500-8 type residues, in parent equivalents, are 0.01 ppm for milk and 0.05 ppm for tissues. Independent method validation data for the HPLC/UV and LC/MS/MS methods are acceptable. Radiovalidation data submitted for the GC/MS and LC/MS/MS methods are adequate for liver and milk, and marginal for muscle. Method 446 has been forwarded to ACB/BEAD for petition method validation. However, following the SOP (ACB-019) for reviewing tolerance methods (September 15, 2008), HED has determined that Method 446 is suitable as an enforcement method (PP#s 8F7385, 8F7390, and 8E7394; DP Num 343700; B. O'Keefe; 9/7/07).

For enforcing tolerances on poultry commodities, BASF has purposed use of a LC/MS/MS Method D9902, which is similar to the method for ruminant commodities (LC/MS/MS Method 446/1). Method D9902 is also a common moiety method that includes a base hydrolysis step. The principle difference between the two methods is that Method D9902 determines residues of pyraclostrobin and its metabolites convertible to BF 500-5 or BF 500-9. BF 500-9 is an isomer of BF 500-8, in which the hydroxyl group is at a different position on the chlorophenyl ring. Adequate method validation data have been provided for Method D9902, and the validated LOQ for each analyte is 0.05 ppm in eggs and poultry tissues, for a combined LOQ of 0.1 ppm. All residues are expressed in parent equivalents. This method was used for data collection in the

MARC Decision Memo, DP# 278044, L. Cheng, 10/9/01
PP#0F6139; DP# 269668, L. Cheng, 11/28/01

The nature of the residue in plants is adequately understood based on acceptable metabolism studies conducted on grapes, potatoes, and wheat. The metabolism of pyraclostrobin is similar in the three crops investigated. Pyraclostrobin and its desmethoxy metabolite (BF 500-3) are the major residues in crop matrices including livestock feeds; tryptophan was found to be the major residue in potato tuber and wheat grain when carbon-14 was introduced in the tolyl ring (*via* the shikimic acid pathway). The major degradation reactions are the removal of the methoxy group from the carbamate nitrogen and breakage of the ether bond.

The HED MARC has determined that for purposes of the tolerance expression and risk assessment, the terminal residues of concern in plants consist of pyraclostrobin and its desmethoxy metabolite (BF 500-3).

860.1300 Nature of the Residue - Livestock

MARC Decision Memo, DP# 278044, L. Cheng, 10/9/01
PP#0F6139; DP# 269668, L. Cheng, 11/28/01

The nature of the residue in livestock is adequately understood based on acceptable ruminant and poultry metabolism studies. In goats, the major residues are pyraclostrobin and BF 500-3 in muscle and fat; parent, BF 500-3, and BF 500-5 and its sulfate conjugate in milk; parent, BF 500-3, and BF 500-5 and its sulfate conjugate, and hydroxylated desmethoxy metabolite (500M67) in kidney; and metabolites hydrolyzed to BF 500-5 and its hydroxylated compound (BF 500-8) in liver. In poultry, the major residues are pyraclostrobin and BF 500-3 in eggs; parent, BF 500-3, and hydroxylated BF 500-3 (500M64) in fat; the glucuronic acid conjugate of hydroxylated BF 500-3 (500M32) in liver. Radioactive residues were below detection in muscle. The main degradation reactions in livestock consist of demethoxylation, hydroxylation, and conjugation, and breaking of the ether bond.

The HED MARC has determined that for the purpose of tolerance and risk assessment, the residues of concern in livestock commodities consist of pyraclostrobin and its metabolites convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol (BF 500-5) and 1-(4-chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol (BF 500-8).

860.1340 Residue Analytical Methods

PP#0F6139; DP# 269668, 11/28/01, L. Cheng
DP# 269850, L. Cheng, 11/8/00
DP# 281042, L. Cheng, 7/26/04

Plant commodities. Two adequate methods were proposed in PP#0F6139 for enforcing tolerance for residues of pyraclostrobin and the metabolite BF 500-3 in/on plant commodities: an LC/MS/MS method (BASF Method D9808) and an HPLC/UV method (Method D9904). The validated method LOQ for both pyraclostrobin and BF 500-3 is 0.02 ppm in all tested plant matrices, for a combined LOQ of 0.04 ppm. Adequate independent method validation and

poultry feeding study. Although Method D9902 has been adequately validated by BASF, an ILV trial and radiovalidation have not been conducted for this method.

Conclusions: An adequate method is available for collecting data and enforcing the proposed tolerances on alfalfa forage and hay. Adequate methods are also available for enforcing the current tolerances on cattle, goat, hog, horse and sheep commodities, and an adequate LC/MS/MS method (BASF Method D9902) is available for determining the residues of concern in poultry commodities. However, an acceptable ILV trial is required for Method D9902 before it can be approved for tolerance enforcement. Separate radiovalidation data are not required for Method D9902, as adequate radiovalidation data are available for Method 446/1 which uses similar sample extraction and purification procedures.

860.1360 Multiresidue Methods

PP#0F6139; DP# 269668, 11/28/01, L. Cheng

Pyraclostrobin was successfully evaluated through several of the FDA protocols, while recovery of BF 500-3 was unsuccessful in all protocols. Pyraclostrobin was completely recovered through Protocol D (in grape) and E (in grape), and partially recovered through Protocol F (in peanut). Metabolite BF 500-3 had poor peak shape and inadequate sensitivity with Protocol C columns, and therefore, was not further analyzed under Protocol D, E, and F. The results of the multiresidue testing for pyraclostrobin were forwarded to FDA on 1/4/02 for the purpose of updating PAM, Volume I.

860.1380 Storage Stability

PP#0F6139; DP# 269668, 11/28/01, L. Cheng

Adequate storage stability data are available indicating that pyraclostrobin and metabolite BF 500-3 are reasonably stable at ≤-10°C in fortified samples of grape juice (juices), sugar beet tops (leafy vegetables), sugar beet roots (root crop), tomatoes (fruit/fruiting vegetable), and wheat grain (non-oily grain) and wheat straw (dry feed) for up to 25 months, and in fortified samples of peanut nutmeats (oilseed) and peanut oil for up to 19 months.

The storage durations and conditions of samples from the crop field trials submitted to support this petition are presented in Table 5.

TABLE 5. Summary of Storage Conditions and Durations of Samples from Alfalfa Field Trials.

Matrix	Storage Temperature (°C)	Actual Storage Duration (Months)	Interval of Demonstrated Storage Stability (Months)
Alfalfa Forage	<-5	5-13	25
Alfalfa Hay	<-5	5-13	25

Conclusions: The storage conditions and durations of alfalfa forage and hay samples from the field trials are supported by the available storage stability data indicating that pyraclostrobin and BF 500-3 are stable in frozen sugar beet tops and wheat straw for at least 25 months.

860.1400 Water, Fish, and Irrigated Crops

There are no proposed/registered uses that are relevant to this guideline topic.

860.1460 Food Handling

There are no proposed/registered uses that are relevant to this guideline topic.

860.1480 Meat, Milk, Poultry, and Eggs

PP#0F6139; DP# 269668, 11/28/01, L. Cheng

Adequate cattle and poultry feeding studies are available. The current tolerances for livestock commodities are based on the residue data from the cattle and poultry feeding studies and the previously calculated dietary burdens of livestock for pyraclostrobin. The maximum dietary burdens for livestock were originally calculated to be 36.3 ppm for beef cattle, 35.4 ppm for dairy cattle, and 0.35 ppm for poultry. Most recently, the dietary burdens for livestock were calculated to be 4.9 ppm for beef cattle, 9.5 ppm for dairy cattle, 0.545 ppm for swine, and 0.945 ppm for poultry (DP# 359194, M. Negussie, 4/02/09).

As alfalfa forage and hay are major livestock feedstuffs, the dietary burdens for livestock were recalculated for this petition. Based on the recent changes in calculating residues in reasonably balanced livestock diets (ChemSAC memo, 6/30/08), the dietary burden for livestock to pyraclostrobin residues was recalculated to be 6.1 ppm for beef cattle, 12.9 ppm for dairy cattle, 2.6 ppm for poultry, and 2.1 ppm for swine (e-mail, J. Stokes, 10/7/09; Table 6).

TABLE 6. Calculation of Maximum Reasonably Balanced Dietary Burdens of Pyraclostrobin Residues for Livestock.

Feedstuff	Type	% Dry Matter	% Diet	Tolerance (ppm)	Dietary Contribution (ppm)
Beef Cattle R 15%, CC 80%, PC 5%					
Alfalfa, hay	R	89	10	30	3.38
Cotton, gin byproducts	R	90	5	30	1.67
Barley, grain	CC	88	50	1.4	0.8
Sorghum, grain, grain	CC	86	25	0.6	0.18
Sugarcane, molasses	CC	75	5	0.4	0.03
Canola/sunflower, meal	PC	92	5	0.3	0.016
TOTAL BURDEN	--	--	100		**6.1**
Dairy Cattle R 45%, CC 45%, PC 10%					
Alfalfa, hay	R	89	20	30	6.75
Sorghum, grain, forage	R	35	25	5.0	3.57
Apple, wet pomace	CC	40	10	8.0	2.0
Barley, grain	CC	88	35	1.4	0.56
Cotton, undelinted seed	PC	90	10	0.3	0.033
TOTAL BURDEN	--	--	100	--	**12.9**
Poultry CC 75%, PC 25%					
Barley, grain	CC	88	75	1.4	1.05
Canola/sunflower, meal	PC	92	20	0.3	0.06

Alfalfa, meal	PC	89	5	30	1.5
TOTAL BURDEN	--	--	100	--	**2.6**
Swine CC 85%, PC 15%					
Barley, grain	CC	88	5	1.4	0.07
Sorghum, grain, grain	CC	86	80	0.6	0.48
Canola/sunflower, meal	PC	92	10	0.3	0.03
Alfalfa, meal	PC	89	5	30	1.5
TOTAL BURDEN	--	--	100	--	**2.1**

Comments:

1) Sugarcane molasses was added to beef diet because of high dry matter. Makes feed more palatable.
2) Alfalfa meal added to poultry and swine diets as some premixed and bagged supplement feeds contain this feedstuff.

Cattle feeding study. In the available cattle feeding study, three groups of dairy cows (3 cows/group) were dosed twice daily with pyraclostrobin for 28 days at levels equivalent to 8.8, 27.2 and 89.6 ppm in their diet. These dose levels are equivalent to 0.7x, 2.1x, and 6.9x the currently calculated dietary burdens.

For the low dose group (0.7x dietary burden), the combined residues of pyraclostrobin and its metabolites convertible to BF 500-5 and BF 500-8 were <LOQ in all samples of whole milk (<0.02 ppm), milk fat (<0.02 ppm), fat (<0.1 ppm), kidney (<0.1 ppm), liver (<0.1 ppm), and muscle (<0.1 ppm). For the mid-dose group (2.1x dietary burden), combined residues were <0.02-<0.024 ppm in milk, <0.02 ppm in skim milk, <0.02-<0.056 ppm in milk fat, <0.1 ppm in fat, kidney and muscle, and 0.464-0.607 ppm in liver. For the high-dose group (6.9x dietary burden), combined residues were 0.038-0.175 ppm in milk (Days 4-27), 0.039-0.102 ppm in skim milk, 0.131-0.258 ppm in milk fat, 0.367-0.396 ppm in kidney, 2.056-2.781 ppm in liver, and <0.1 ppm in fat and muscle.

Poultry feeding study. Three groups of laying hens (4 hens per subgroup with 3-5 subgroups/dose) were orally dosed once daily for 30 consecutive days with pyraclostrobin at dose levels equivalent to 0.28, 0.88 and 3.01 ppm in their diet. These dose levels are respectively equivalent to 0.1x, 0.3x, and 1.1x the currently calculated dietary burden for poultry.

For the high-dose group (1.1x dietary burden) residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 were less than the method LOQ (<0.05 ppm) in all egg and tissue samples, except for one egg sample (Day 17), where residues of pyraclostrobin were detected at 0.064 ppm. However, upon reanalysis, pyraclostrobin residues in this egg sample were <0.05 ppm. Residue analysis of BF 500-8 was not conducted as the metabolism data show all metabolites hydrolyzable to BF 500-8 would be less than 10% of the total radioactive residues (TRR). Instead an isomeric compound (BF 500-9) was measured, and all residues of BF 500-9 were <0.05 ppm in all egg and tissue samples.

Conclusions: Based on the calculated dietary exposure of dairy cattle (12.9 ppm) and the residue data from the mid-dose group (27.2 ppm; 2.1x level) in the cattle feeding study, the maximum expected combined pyraclostrobin residues in ruminant commodities would be <0.024 ppm in milk, <0.056 ppm in milk fat, <0.1 ppm in kidney, muscle and fat, and 0.289 ppm in liver. These

data indicate that the existing tolerances of 0.1 ppm for milk, fat, and meat, 1.5 ppm for liver, and 0.2 ppm for meat byproducts, except liver will not need to be increased by the proposed use on alfalfa.

Based on the calculated dietary exposure of swine (2.1 ppm) and the residue data from the low-dose group (8.8 ppm; 4.1x level) in the cattle feeding study, the maximum expected combined pyraclostrobin residues would be <LOQ in all hog commodities. Based on the mid-dose group (27.2 ppm; 13.0x level), combined pyraclostrobin residues would also be <LOQ in hog fat, meat, and liver at a 13.0x feeding level. The tolerances for pyraclostrobin on swine will not be increased by the proposed use on alfalfa.

Based on the recalculated dietary burden for poultry (2.6 ppm), the high-dose group in the poultry feeding study is now considered to be equivalent to 1.1x the poultry dietary burden. The combined residues of pyraclostrobin and its metabolites convertible to BF 500-5 and BF 500-9 were <LOQ in eggs and all tissues; however, because there is no dose group in the feeding study representing a 10x feeding level, ARIA can no longer verify that residues in poultry commodities represent a Category 180.6(a)(3) situation.

To further assess the need for tolerances, ARIA and HED re-examined the data from the poultry metabolism studies, in which hens were dosed at levels equivalent to 12.1-12.7 ppm in the diet (~4.8x dietary burden) for 7 consecutive days. For poultry fat and liver, which had TRRs of 0.065-0.083 ppm and 0.317-0.474 ppm respectively, the identified residues of pyraclostrobin and its metabolites potentially convertible to BF 500-5 or BF 500-9 were totaled for both matrices. At dose levels equivalent to ~4.8x the poultry dietary burden, combined pyraclostrobin residues were estimated to be 0.041-0.042 ppm in fat and 0.082-0.143 ppm in liver. When extrapolated to a 10x feeding level, combined residues could be 0.088ppm in fat and 0.299 ppm in liver. As the combined residues of concern could be at or above the method LOQ (0.1 ppm) in the poultry fat and liver following only 7 days of dosing at a 10x level, it is not possible to establish with certainty whether finite residues will be incurred in poultry fat and meat byproduct, but there is a reasonable expectation of finite residues. Therefore, tolerances should be established for poultry fat and meat byproducts at the proposed enforcement method LOQ (0.1 ppm).

The levels of the TRR in muscle were ≤0.009 ppm and in eggs were ≤0.037 ppm at a ~4.8x feeding level. Considering the levels of the TRR levels in muscle (≤0.009 ppm) and eggs (≤0.037 ppm) at a ~4.8x feeding level, quantifiable levels (≥0.1 ppm) of the residues of concern would normally not be expected to occur in eggs and poultry meat at a 10x feeding level. However, as the poultry metabolism study was only conducted for 7 days and the TRRs may not have reached a plateau, it is not possible to establish with certainty whether finite residues will not be incurred in poultry meat and eggs. Therefore, tolerances for egg and poultry meat should be established at the proposed enforcement method LOQ (0.1 ppm). **A revised Section F for the residues of pyraclostrobin on poultry meat, fat and meat byproducts, and eggs at 0.1 ppm is required.**

860.1500 Crop Field Trials

MRID 47584401, W. Cutchin, in process

BASF submitted field trial data on alfalfa in support of a new use for pyraclostrobin (EC) on alfalfa. Twelve alfalfa field trials were conducted in the United States in Zones 1, 2, 5, 7, 9, 10, and 11 and Canada in Zones 5 and 5B during the 2007 growing season. Each test site included one control plot and four treated plots (Treatments #2-5) that varied the number of pyraclostrobin applications (2 or 3) and the treatment to harvest intervals (14 or 21 days). For Treatments #2 and #3, pyraclostrobin (12.8% WDG) was applied to alfalfa as three broadcast foliar applications during vegetative development at rates of 0.142-0.161 lb ai/A, for total rates of 0.44-0.47 lb ai/A. For Treatment #2, the targeted timings for the three applications were 28 and 14 days before the 1st cutting and 14 days before the 2nd cutting. For Treatment #3, the targeted timings for the three applications were 35 and 21 days before the 1st cutting and 21 days before the 2nd cutting. The two RTIs were 12-15 days and 28-53 days for Treatment #2 and 13-14 days and 29-53 days for Treatment #3. For Treatments #4 and #5, pyraclostrobin (12.8% WDG) was applied to alfalfa as two broadcast foliar applications during vegetative development at rates of 0.141-0.163 lb ai/A and RTIs of 28-53 days, for total rates of 0.29-0.31 lb ai/A. The targeted timings for the two applications were 14 days before the 1st and 2nd cuttings for Treatment #4 and 21 days before the 1st and 2nd cuttings for Treatment #5. All applications were made using ground equipment at volumes of 20-34 gal/A, and included the use of adjuvants.

With the exception of one test site, three cuttings of alfalfa were harvested from each plot according to typical agricultural practices, with the 3rd cutting being made at normal maturity (beginning bloom stage). The exact treatment-to-harvest intervals for each cutting are presented below along with the residue levels in forage and hay. At each cutting, single control and duplicate treated samples of alfalfa forage and hay were collected from each test, with hay samples being field-dried to a moisture content of ~10-20% prior to sampling. After sampling, forage and hay samples were held in frozen (<-5°C) storage for up to 13 months prior to extraction for analysis. This duration is supported by the available storage stability data.

Samples of alfalfa forage and hay were analyzed for residues of pyraclostrobin and its desmethoxy metabolite BF 500-3 using an adequate LC/MS/MS method (BASF Method D9908). The validated LOQ is 0.02 ppm for each analyte in forage and hay, and the LOQ for combined residues is 0.04 ppm.

For Treatment #2 (3 applications each at ~0.15 lb ai/A with ~14-day PHI), combined residues of pyraclostrobin and BF 500-3 in/on forage were 0.44-7.24 ppm at 12-15 days after the second application (1st cutting), 0.85-8.15 ppm at 12-16 days after the third application (2nd cutting), and <0.04-0.24 ppm at 43-73 days after the third application (3rd cutting). Combined residues in/on hay were 1.42-20.49 ppm at 12-15 days after the second application (1st cutting), 4.02-22.87 ppm at 12-16 days after the third application (2nd cutting), and 0.05-0.87 ppm at 43-73 days after the third application (3rd cutting). For the 1st, 2nd, and 3rd cuttings, combined residues respectively averaged 2.99, 2.69 and 0.09 ppm in/on forage and 7.84, 9.28 and 0.27 ppm in/on hay.

For Treatment #3 (3 applications each at ~0.15 lb ai/A with ~21-day PHI), combined residues in/on forage were 0.06-3.38 ppm at 19-23 days after the second application (1st cutting), 0.30-2.59 ppm at 20-23 days after the third application (2nd cutting), and <0.04-0.18 ppm at 49-76 days after the third application (3rd cutting). Combined residues in/on hay were 0.08-18.75 ppm at 19-23 days after the second application (1st cutting), 1.31-8.01 ppm at 20-23 days after the third application (2nd cutting), and <0.04-0.59 ppm at 49-76 days after the third application (3rd

cutting). For the 1st, 2nd, and 3rd cuttings, combined pyraclostrobin residues respectively averaged 0.89, 1.15 and 0.08 ppm in/on forage and 3.44, 3.57 and 0.20 ppm in/on hay.

For Treatment #4 (2 applications each at ~0.15 lb ai/A with ~14-day PHI), combined pyraclostrobin residues in/on forage were 0.40-5.94 ppm at 12-15 days after the first application (1st cutting), 0.57-6.56 ppm at 12-16 days after the second application (2nd cutting), and <0.04-0.18 ppm at 43-70 days after the second application (3rd cutting). Combined residues in/on hay were 1.28-15.83 ppm at 12-15 days after the first application (1st cutting), 2.77-18.81 ppm at 12-16 days after the second application (2nd cutting), and 0.05-0.46 ppm at 43-70 days after the second application (3rd cutting). For the 1st, 2nd, and 3rd cuttings, combined residues respectively averaged 2.31, 2.65 and 0.08 ppm in/on forage and 7.44, 8.59 and 0.18 ppm in/on hay.

For Treatment #5 (2 applications each at ~0.15 lb ai/A with ~21-day PHI), combined residues in/on forage were <0.04-3.03 ppm at 19-23 days after the first application (1st cutting), 0.23-2.87 ppm at 20-23 days after the second application (2nd cutting), and <0.04-0.20 ppm at 49-76 days after the second application (3rd cutting). Combined residues in/on hay were 0.20-10.48 ppm at 19-23 days after the first application (1st cutting), 1.47-12.21 ppm at 20-23 days after the second application (2nd cutting), and <0.04-0.56 ppm at 46-76 days after the second application (3rd cutting). For the 1st, 2nd, and 3rd cuttings, combined pyraclostrobin residues respectively averaged 0.80, 1.12 and 0.08 ppm in/on forage and 2.61, 3.90 and 0.20 ppm in/on hay.

Overall, combined pyraclostrobin residues were higher in forage and hay from the treatments using 3 applications rather than 2 applications, and the residues were higher in forage and hay from treatments having the ~14-day PHI rather than the ~21-day PHI. The worse-case treatment was Treatment #2, and the highest residues in forage and hay were found in the 1st and 2nd cuttings. For Treatment #2, average combined residues from the 1st and 2nd cuttings were 2.99 and 2.69 ppm for forage and 7.84 and 9.28 ppm for hay.

TABLE 7. Summary of Combined Residue Data from Alfalfa Field Trials with Pyraclostrobin (WDG).

Commodity	Total Applic. Rate (lb ai/A)	Trt. No.[1]	Cutting	PHI (days)	Combined Residue Levels (ppm)[2]						
					n	Min.	Max.	HAFT[3]	Median	Mean	Std. Dev.
Alfalfa (proposed use = 0.44 lb ai/A total application rate, 14-day PHI)											
Alfalfa Forage	**0.44-0.47**	**2[4]**	**1st**	**12-15**	**24**	**0.44**	**7.24**	**6.69**	**2.07**	**2.99**	**2.02**
			2nd	**12-16**	**24**	**0.85**	**8.15**	**7.41**	**1.55**	**2.69**	**1.97**
			3rd	43-73	22	<0.04	0.24	0.21	0.07	0.09	0.06
	0.45-0.47	3	1st	19-23	24	0.06	3.38	3.21	0.79	0.89	0.81
			2nd	20-23	24	0.30	2.59	2.47	0.97	1.15	0.72
			3rd	49-76	22	<0.04	0.18	0.18	0.06	0.08	0.04
	0.29-0.31	4	1st	12-15	24	0.40	5.94	5.35	1.91	2.31	1.56
			2nd	12-16	24	0.57	6.56	6.42	1.97	2.65	1.77
			3rd	43-70	22	<0.04	0.18	0.18	0.05	0.08	0.05
	0.30-0.31	5	1st	19-23	24	<0.04	3.03	3.00	0.67	0.80	0.79
			2nd	20-23	24	0.23	2.87	2.78	1.03	1.12	0.63
			3rd	49-76	22	<0.04	0.20	0.20	0.05	0.08	0.05
Alfalfa Hay	**0.44-0.47**	**2[4]**	**1st**	**12-15**	**24**	**1.42**	**20.49**	**19.77**	**6.60**	**7.84**	**5.27**

TABLE 7. Summary of Combined Residue Data from Alfalfa Field Trials with Pyraclostrobin (WDG).

Commodity	Total Applic. Rate (lb ai/A)	Trt. No.[1]	Cutting	PHI (days)	Combined Residue Levels (ppm)[2]						
					n	Min.	Max.	HAFT[3]	Median	Mean	Std. Dev.
			2nd	**12-16**	**24**	**4.02**	**22.87**	**22.19**	**7.07**	**9.28**	**5.47**
			3rd	43-73	22	0.05	0.87	0.64	0.22	0.27	0.23
	0.45-0.47	3	1st	19-23	24	0.08	18.75	16.87	2.27	3.44	4.45
			2nd	20-23	24	1.31	8.01	7.72	3.56	3.57	1.89
			3rd	49-76	22	<0.04	0.59	0.52	0.15	0.20	0.18
	0.29-0.31	4	1st	12-15	24	1.28	15.83	15.28	6.37	7.44	4.44
			2nd	12-16	24	2.77	18.81	17.93	7.86	8.59	4.51
			3rd	43-70	22	0.05	0.46	0.42	0.12	0.18	0.13
	0.30-0.31	5	1st	19-23	24	0.20	10.48	9.88	1.72	2.61	2.80
			2nd	20-23	24	1.47	12.21	10.70	3.18	3.90	2.34
			3rd	49-76	22	<0.04	0.56	0.51	0.13	0.20	0.17

[1] Treatments #2 and #3 included three pyraclostrobin applications at ~0.145 lb ai/A/application with the first and second applications made prior to the 1st cutting and the final application made prior to the 2nd cutting. Treatments #4 and #5 included two applications at ~0.145 lb ai/A/application, with the first application made prior to the 1st cutting and the second application made prior to the 2nd cutting.

[2] The combined LOQ for residues of pyraclostrobin and BF 500-3 is 0.04 ppm. For purposes of calculating median and mean and standard deviation, the LOQ (0.04 ppm) was used for residue values <LOQ.

[3] HAFT = Highest Average Field Trial.

[4] The residue data used to calculate tolerances for forage and hay are **bolded**.

Conclusions: The submitted alfalfa field trial data are adequate and will support the use of pyraclostrobin, formulated as a WDG, for foliar applications to alfalfa. An adequate number of tests were conducted on alfalfa in the appropriate geographic regions, and the tests were conducted at ~1x the proposed use rate. Samples were collected around the proposed PHI and analyzed for residues of both parent and metabolite BF 500-3 using an adequate LC/MS/MS method. The field trial data are also supported by the available storage stability data. The available field trial data support tolerances of 10 ppm for alfalfa forage and 30 ppm for alfalfa hay. **A revised Section F for the residues of pyraclostrobin on alfalfa forage at 10 ppm and hay at 30 ppm is required.**

Although no field trial data were submitted reflecting use of the proposed EC formulation, previously submitted side-by-side field trials on tomatoes, cucumbers, and grapes comparing WDG and EC formulations of pyraclostrobin have shown that residues resulting from the two types of formulations are similar (DP# 269668, L. Cheng, 11/28/01). Therefore, the available data for the WDG formulation will also cover the use of the EC formulations on alfalfa.

Field trial data were not submitted to support the proposed seed treatment use on alfalfa; however, no seed treatment residue data are required as the seed treatment rate is negligible compared to the proposed foliar applications. Based on typical seeding rates for alfalfa (2-20 lb seed/A), the maximum seed treatment rate (0.04 lb ai/100 lb seed) would be equivalent to a field use rate of 0.008 lb ai/A, compared to the maximum foliar rate of 0.44 lb ai/A.

860.1520 Processed Food and Feed

HED does not require residue data for any processed commodities associated with alfalfa. Therefore, data requirements for processed food and feed are not relevant to this tolerance petition.

860.1650 Submittal of Analytical Reference Standards

Analytical reference standards for pyraclostrobin (with an expiration date of 2/1/10) and its desmethoxy metabolite (with an expiration date of 11/1/11) are currently available in the EPA National Pesticide Standards Repository (personal communication with Dallas Wright; ACB/BEAD; 7/22/09). **However, analytical standards are not currently available for the common moiety analytes (BF 500-5, BF 500-8 and BF 500-9) determined by the tolerance enforcement methods for animal commodities. Analytical reference standards for these three analytes must be supplied and supplies replenished as requested by the Repository.** The reference standards should be sent to the Analytical Chemistry Lab, which is located at Fort Meade, to the attention of either Theresa Cole or Frederic Siegelman at the following address:

USEPA
National Pesticide Standards Repository/Analytical Chemistry Branch/OPP
701 Mapes Road
Fort George G. Meade, MD 20755-5350

(Note that the mail will be returned if the extended zip code is not used.)

860.1850 Confined Accumulation in Rotational Crops

MARC Decision Memo, DP# 278044, L. Cheng, 10/9/01
PP#0F6139; DP# 269668, L. Cheng, 11/28/01

An adequate confined rotational crop study is available indicating that the metabolism of pyraclostrobin in rotated crops is similar but more extensive than that in primary crops. Pyraclostrobin undergoes demethoxylation to yield BF 500-3, followed by further degradation to medium polar and polar metabolites, and subsequent conjugation reactions and incorporation into natural products. The HED MARC has determined that the residues of concern in rotational crops consist of pyraclostrobin and metabolite BF 500-3.

860.1900 Field Accumulation in Rotational Crops

PP#0F6139; DP# 269668, L. Cheng, 11/28/01

A limited field rotational crop study indicates that residues of pyraclostrobin and metabolite BF 500-3 were each less than the method LOQ (<0.02 ppm) in/on rotational crop matrices (radish, roots and tops; cabbage, with and without wrapper leaves; and wheat forage, hay, and grain) planted 14 days following the last of six sequential foliar applications to the primary crop, cucumbers, of the 2 lb/gal EC formulation at 0.19-0.20 lb ai/A/application (~1.2 lb ai/A/season). Residues of pyraclostrobin in/on one sample of wheat straw from the CA test site were at the

LOQ (0.02 ppm), but residues of pyraclostrobin in/on a replicate sample from the same plot were below the LOQ (0.012 ppm) for an average residue of <0.02 ppm. Residues of metabolite BF 500-3 were nondetectable (<0.02 ppm) in/on all samples of wheat straw.

The registered pyraclostrobin end-use product labels presently specify a 14-day plant-back interval restriction for all crops that are not registered. No additional rotational crop data are required to support the purposed use on alfalfa.

860.1550 Proposed Tolerances

For purposes of both the tolerance expression and dietary risk assessment, HED has concluded that the residues of concern in plant commodities include pyraclostrobin and it desmethoxy metabolite, BF 500-3. The residues of concern in livestock include pyraclostrobin and its metabolites convertible to BF 500-5 and BF 500-8. Tolerances are currently established for the combined residues of pyraclostrobin and BF 500-3, expressed as parent, in plant commodities at levels ranging from 0.02 ppm in/on wheat grain to 30 ppm in/on cotton gin byproducts [40 CFR §180.582(a)(1)]. Tolerances for livestock commodities are established for the combined residues of pyraclostrobin and its metabolites convertible to BF 500-5 and BF 500-8, each expressed as parent, at levels ranging from 0.1 ppm in milk, meat, and fat to 1.5 ppm in liver of cattle, goats, hogs, and sheep [40 CFR §180.582(a)(2)]. No tolerances are established for poultry commodities or rotational crops. The tolerances being proposed by BASF for the current petition are listed in Table 8, along with ARIA's recommended tolerances.

It is recommended that the tolerance expressions [40 CFR § 180.474(a)(1), 40 CFR §180.474 (a)(2), and 40 CFR §180.474 (b)] be amended to reflect the new *Interim Guidance on Tolerance Expressions* (S. Knizner, 05/27/09). The existing language for 40 CFR § 180.582(a)(1) is:

(a) General. (1) Tolerances are established for combined residues of the fungicide expressed as parent compound, in or on the following raw agricultural commodities.

The above quoted phrase should be replaced with the following:

a) General. (1) Tolerances are established for residues of the fungicide pyraclostrobin, including its metabolites and degradates, in or on the commodities in the table below. Compliance with the tolerance levels specified below is to be determined by measuring only the sum of pyraclostrobin (carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester) and its desmethoxy metabolite (methyl-N-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenylcarbamate), calculated as the stoichiometric equivalent of pyraclostrobin, in or on the commodity.

The existing language for 40 CFR § 180.582(a)(2) is

(2) Tolerances are established for combined residues of the fungicide pyraclostrobin (carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester) and its metabolites convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol and 1-(4-chloro-2-

hydroxyphenyl)-1H-pyrazol-3-ol, expressed as parent compound, in or on the following raw agricultural commodities.

The above quoted phrase should be replaced with the following:

(2) Tolerances are established for residues of the fungicide pyraclostrobin, including its metabolites and degradates, in or on the commodities in the table below. Compliance with the tolerance levels specified below is to be determined by measuring only those pyraclostrobin (carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester) residues convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol and 1-(4-chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol, expressed as the stoichiometric equivalent of pyraclostrobin, in or on the commodity.

The existing language for 40 CFR § 180.582(b) is

(b) Section 18 emergency exemptions. A time-limited tolerance is established for combined residues of the fungicide pyraclostrobin, (carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl] phenyl]methoxy-, methyl ester) and its desmethoxy metabolite (methyl-N-[[[1-(4-chlorophenyl) pyrazol-3-yl]oxy]o-tolyl]carbamate) in connection with use of the pesticide under section 18 emergency exemptions granted by EPA. The time-limited tolerance will expire and is revoked on the date specified in the following table.

The above quoted phrase should be replaced with the following:

(b) Section 18 emergency exemptions. A time-limited tolerance is established for residues of the fungicide pyraclostrobin, including its metabolites and degradates, in or on the commodities in the table below. Compliance with the tolerance levels specified below is to be determined by measuring only those pyraclostrobin (carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester) residues convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol and 1-(4-chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol, expressed as the stoichiometric equivalent of pyraclostrobin, in or on the commodity in connection with use of the pesticide under section 18 emergency exemptions granted by EPA. The time-limited tolerance will expire and is revoked on the date specified in the following table.

Note to PM: The tolerance for horse liver was established at 0.1 ppm in 40CFR 180.582(a)(2). However, the tolerance was established in error. The body of the FR Notice indicates that the tolerance was intended to be 1.5 ppm while the final table lists 0.1 ppm ([FR Doc. 02-24487, Filed 9/26/02). This should be corrected.

An adequate number of alfalfa field trials conducted at ~1x the proposed use rate are available to support permanent tolerances. The Agency's SOP "*Guidelines for Setting Pesticide Tolerances Based on Field Trial Data*" was utilized for determining the appropriate tolerances (Appendix II). For alfalfa forage and hay, residue data from both the 1st and 2nd cuttings of Treatment #2 (1x rate) were used to assess tolerances as both cuttings were collected around the proposed 14-day PHI, and residue levels were similar for the two cuttings. The recommended tolerances for alfalfa forage and hay are 10 and 30 ppm, respectively.

TABLE 8. Tolerance Summary for Pyraclostrobin.

Commodity	Proposed/ Established Tolerance (ppm)	Recommended Tolerance (ppm)	Comments; *Correct Commodity Definition*
Eggs	None	0.1	

[1] For poultry commodities, tolerances should be expressed as the combined residues of the pyraclostrobin and its metabolites convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol (BF 500-5) and 1-(3-chloro-4-hydroxyphenyl)-1H-pyrazol-3-ol (BF 500-9), expressed as parent compound.

References

DP Number: 269850
Subject: PP# 0F06139. Pyraclostrobin (BAS 500F) in or on Various Crops. Request for Tolerance Method Validation (TMV) Trial.
From: L. Cheng
To: F. D. Griffith, Jr.
Dated: 11/8/00
MRIDs: 45118505, 45118504, 45118509, 45118510, 45118501, 45118503, 45118507, 45118514

DP Number: 278044
Subject: PP# 0F06139. PC Code 099100. Pyraclostrobin. Outcome of the HED Metabolism Assessment Review Committee (MARC) Meeting Held on September 20, 2001.
From: L. Cheng
To: Y. Donovan
Dated: 10/09/01
MRIDs: None

DP Numbers: 269668, 272771, 272789, 274095, 274192, 274471, 274957, 275843, and 278429
Subject: PP#0F06139. Pyraclostrobin on Various Crops: Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits, Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean), Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits, Strawberry, Sugar Beet, Tree Nuts, Tuberous and Corm Vegetables, and Wheat. Review of Analytical Methods and Residue Data.
From: L. Cheng
To: C. Giles-Parker/J. Bazuin
Dated: 11/28/01
MRIDs: 45118428-451184-37, 45118501-45118512, 45118514-45118537, 45118601-45118625, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and 45429901

With regards to the current tolerances for livestock commodities, the existing tolerances are adequate for milk, meat, fat, liver, and meat byproducts (except liver) of cattle, goats, horses, sheep and hogs.

Based on the recalculated dietary burden for poultry and data from the poultry feeding and metabolism studies, it is not possible to establish with certainty whether finite residues will be incurred in poultry commodities, but the residues of concern could occur ≥LOQ at a 10x feeding level. Therefore, tolerances should be established for poultry meat, fat and meat byproducts, and eggs at the proposed enforcement method LOQ (0.1 ppm). The tolerances for poultry commodities should be established under 180.582(a)(3), and the tolerance expression should read as follows:

> "Tolerances are established for the combined residues of the fungicide pyraclostrobin carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester and its metabolites convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol and 1-(3-chloro-4-hydroxyphenyl)-1H-pyrazol-3-ol, expressed as parent compound, in or on the following raw agricultural commodities."

There are currently no proposed or established Codex, Canadian, or Mexican Maximum Residue Limits (MRLs) for residues of pyraclostrobin on alfalfa (Appendix I). However, there are Canadian MRLs for various livestock commodities, including poultry meat, meat byproducts and eggs. The U.S. tolerance and Canadian MRL expressions are the same for both plant and livestock commodities, but several of the recommended changes in tolerances on livestock commodities will result in differences between the U.S. tolerances and the respective Canadian MRLs.

TABLE 8. Tolerance Summary for Pyraclostrobin.

Commodity	Proposed/ Established Tolerance (ppm)	Recommended Tolerance (ppm)	Comments; *Correct Commodity Definition*
40 CFR 180.582(a)(1)			
Alfalfa, Forage	9	10	Adequate alfalfa forage and hay residue data are available. The tolerances were calculated using the tolerance harmonization spreadsheet and the residue data from the 1st and 2nd cuttings of Treatment #2.
Alfalfa, Hay	27	30	
40 CFR 180.582(a)(3) [1]			
Poultry, fat	None	0.1	Based on the calculated dietary burden for poultry and the data from the poultry feeding and metabolism studies, tolerances are required at the method LOQ.
Poultry, meat byproducts	None	0.1	
Poultry, meat	None	0.1	

Appendix I – International Residue Limits

INTERNATIONAL RESIDUE LIMIT STATUS

Chemical Name: methyl [2-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl] phenyl]methoxycarbamate	Common Name: Pyraclostrobin	X Proposed tolerances 9 Reevaluated tolerances 9 Other	Date: 8/12/09

Codex Status (Maximum Residue Limits)	U. S. Tolerances
□ No Codex proposal step 6 or above X No Codex proposal step 6 or above for the crops requested	Petition Number: PP#9F7528 DP#: 367409 Other Identifier:
Residue definition (step 8/CXL): Pyraclostrobin	Reviewer/Branch: J. Redden/RAB3
	Residue definitions: *Plant commodities: combined residues of* pyraclostrobin and BF 500-3, expressed as parent Animal commodities: Combined residues of pyraclostrobin and its metabolites convertible to BF 500-5 and BF 500-8 (or BF 500-9 for *poultry),expressed as parent*

Crop (s)	MRL (mg/kg)	Crop(s)	Recommended Tolerance (ppm)
		Alfalfa, forage	10
		Alfalfa, hay	30
		Poultry, fat	0.1
		Poultry, meat byproducts	0.1
		Hog, meat byproducts	0.1

Limits for Canada	**Limits for Mexico**
□ No Limits X Proposed Limits for the crops requested	X No Limits □ No Limits for the crops requested
Residue definition: Animal commodities: Combined residues of pyraclostrobin and its metabolites convertible to *BF 500-5 and BF 500-8 (or BF 500-9 for* poultry),expressed as parent	Residue definition: NA

Crop(s)	MRL (mg/kg)	Crop(s)	MRL (ppm)
Fat of cattle goats, hogs, horses and sheep	0.1		
Liver of cattle, goats, hogs, horses and sheep	1.5		
Meat byproducts (except liver) of cattle, goats, hogs, horses and sheep	0.2		
Meat byproducts of poultry	0.1		
Meat of cattle, goats, hogs, horses, poultry and sheep	0.1		
Milk	0.1		
Notes/Special Instructions:			

DP Numbers: 281042, 286732, 287729, 288459, 290342, 290343, 290369, 292440, 293088, 293684, 295893, and 298178

Subject: Pyraclostrobin. PP#3F06581, 2F06431, 2E6473, 3E6548, 3E6553, 3E6774, and 2F06139. Petitions for the establishment of permanent tolerances to allow uses on corn (field, sweet, and pop), hops, mint, pome fruits, edible-podded legume vegetables, succulent peas, sunflower, *Brassica* leafy greens, soybeans, succulent beans, broccoli, cabbage, lettuce (head and leaf), spinach, celery, turnip greens, and the import commodities mango and papaya. Application for amended Section 3 registration for citrus (reduced PHI). Petitioner's response to data deficiencies identified in PP#0F06139 regarding storage stability data, dried shelled peas and beans (reduced PHI), and uses on dry and succulent peas. Summary of Analytical Chemistry and Residue Data..

From: L. Cheng

To: C. Giles-Parker/J. Bazuin

Dated: 7/26/04

MRIDs: 45596211, 45623406, 45623407, 45623408, 45623410, 45645801, 45645802, 45645803, 45645804, 45702901, 45765401, 45832001, 45858801, 45858802, 45903601, 45903602, 46033901-04, 46084401-04, 46109101, 46109102

DP Number: 359194

Subject: Pyraclostrobin: Petitions for the Establishment of Permanent Tolerances on Grain, Sorghum Grain, Forage and Stover (PP#8F7385); Increase of Tolerance for the Stone Fruit Crop Group 12 to satisfy European Union (EU) import requirement (PP#8F7390); and Establishment of a Permanent import Tolerance for Coffee (PP#8E7394). Summary of Analytical Chemistry and Residue Data.

From: M. Negussie

To: T. Kish

Dated: 4/2/09

MRIDs: 47470201 through 47470204

Attachments:

Appendix I – International Residue Limit Status sheet

Appendix II - Tolerance Assessment Calculations

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Appendix II. Tolerance Assessment Calculations.

The dataset used to establish tolerances for pyraclostrobin on alfalfa forage and hay consisted of field trial data representing three applications of pyraclostrobin (WDG) at rates of 0.14-0.15 lb ai/A (~0.44 lb ai/A/season) and a 14-day PHI. The residues from the 1st and 2nd cuttings of treatment #2 had similar range of residue values, and were combined for the tolerance calculations. As specified by the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data* SOP, the field trial application rates and PHIs were within 25% of the maximum label application rate and minimum label PHI, respectively. The residue values used to calculate the tolerance are provided in Table II-1. Residues were above the method LOQ (0.02 ppm) in/on all 24 samples of forage and 24 samples of hay.

The forage and hay datasets were entered into the tolerance spreadsheet. Visual inspection of the lognormal probability plots (Figures II-1 and II-3) provided in the spreadsheet indicate that the datasets are reasonably lognormal. The result from the approximate Shapiro-Francia test statistic (Figures II-2 and II-4) confirmed that the assumption of log normality should not be rejected.

Since the field trial data for pyraclostrobin on alfalfa forage and hay represent large datasets (≥15 samples) and are reasonably lognormal, the minimum of the 95% upper confidence limit (UCL) on the 95th percentile and the point estimate of the 99th percentile was selected as the tolerance value. For alfalfa forage, the 95% UCL on the 95th percentile was 10 ppm and the point estimate of the 99th percentile was 12 ppm (Figure II-2); therefore, 10 ppm is the recommended tolerance level for alfalfa forage. For alfalfa hay, the 95% UCL on the 95th percentile was 30 ppm and the point estimate of the 99th percentile was 35 ppm (Figure II-2); therefore, 30 ppm is the recommended tolerance level for alfalfa hay.

Table II-1.	**Pyraclostrobin Residues in/on Alfalfa Forage and Hay following Three Foliar Applications of Pyraclostrobin (WDG) at Rates Totaling ~0.43 lb ai/A/season.**			
Regulator:	EPA		EPA	
Chemical:	Pyraclostrobin		Pyraclostrobin	
Crop:	Alfalfa Forage		Alfalfa Hay	
PHI:	12-15 days (Cuttings 1+2)		12-15 days (Cuttings 1+2)	
App. Rate:	3 at 0.14-0.15 lb ai/A		3 at 0.14-0.15 lb ai/A	
Submitter:	BASF		BASF	
MRID Citation:	MRID 47584401		MRID 47584401	
	Combined Residues		**Combined Residues**	
	0.44	2.04	1.42	6.98
	0.50	2.05	1.55	7.06
	0.57	2.08	2.70	7.07
	0.85	2.27	3.17	7.33
	0.89	2.47	3.49	8.46
	1.11	2.63	3.53	8.58
	1.23	2.95	3.70	8.61
	1.27	2.95	4.02	8.79
	1.37	3.10	4.24	9.07
	1.37	3.33	4.32	9.29
	1.40	3.73	4.78	9.52
	1.40	3.94	4.79	10.44
	1.42	4.20	4.79	11.38
	1.42	4.49	4.92	11.62
	1.48	4.57	5.47	12.07
	1.53	5.37	5.57	13.39
	1.56	5.43	5.63	13.63
	1.73	5.45	5.96	15.00
	1.75	5.72	6.13	17.29
	1.76	6.13	6.33	18.73
	1.81	6.57	6.33	19.04
	1.83	6.67	6.41	20.49
	1.96	7.24	6.51	21.50
	2.01	8.15	6.79	22.87

Figure II-1. Lognormal Probability Plot of Combined Pyraclostrobin Residues in/on Alfalfa Forage Following Three Foliar Applications Totaling ~0.44 lb ai/A.

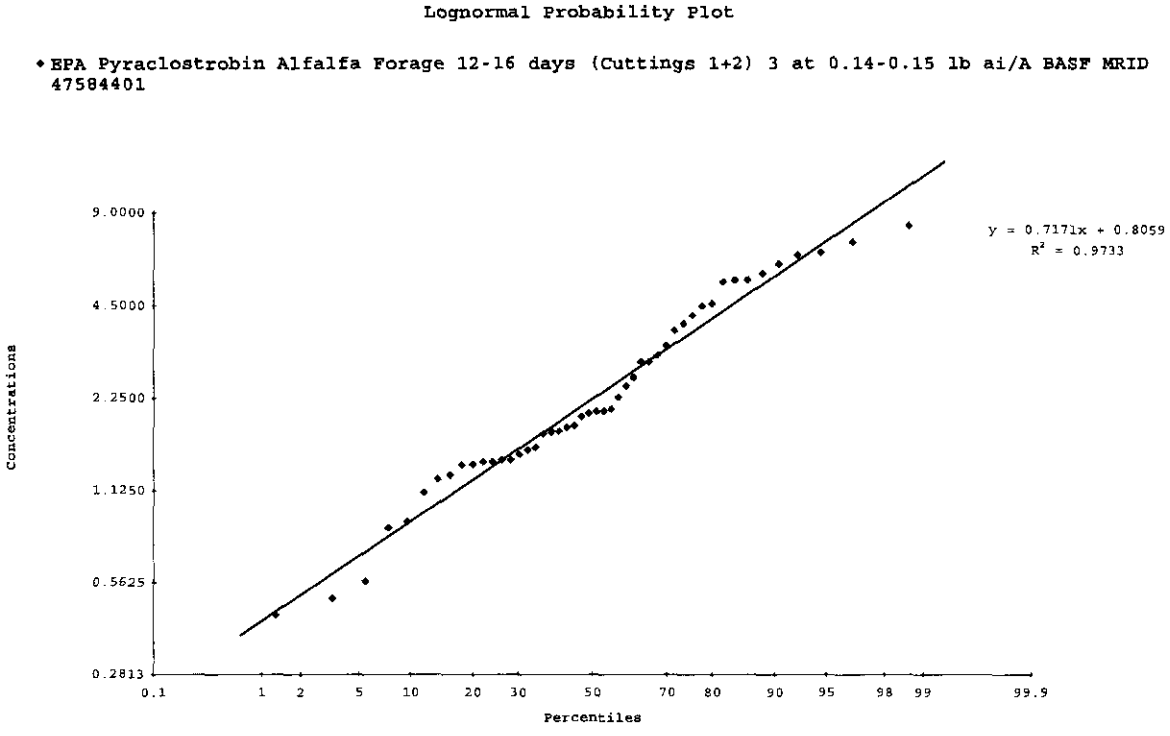


Figure II-2. Data Summary Sheet for Combined Pyraclostrobin Residues in/on Alfalfa Forage Following Three Foliar Applications Totaling ~0.44 lb ai/A.

Regulator:	EPA
Chemical:	Pyraclostrobin
Crop:	Alfalfa Forage
PHI:	12-16 days (Cuttings 1+2)
App. Rate:	3 at 0.14-0.15 lb ai/A
Submitter:	BASF
MRID Citation:	MRID 47584401
n:	48
min:	0.44
max:	8.15
median:	2.03
average:	2.84

	95th Percentile	99th Percentile	99.9th Percentile
EU Method I Normal	7.0 (7.0)	8.0 (9.0)	9.0 (--)
EU Method I Log Normal	8.0	12 (18)	25 (--)
EU Method II Distribution-Free		9.0	
California Method $\mu + 3\sigma$		9.0	
UPLMedian95th		11	
Approximate Shapiro-Francia Normality Test		0.9733 p-value > 0.05 : Do not reject lognormality assumption	

Figure II-3. Lognormal Probability Plot of Combined Pyraclostrobin Residues in/on Alfalfa Hay Following Three Foliar Applications Totaling ~0.44 lb ai/A.

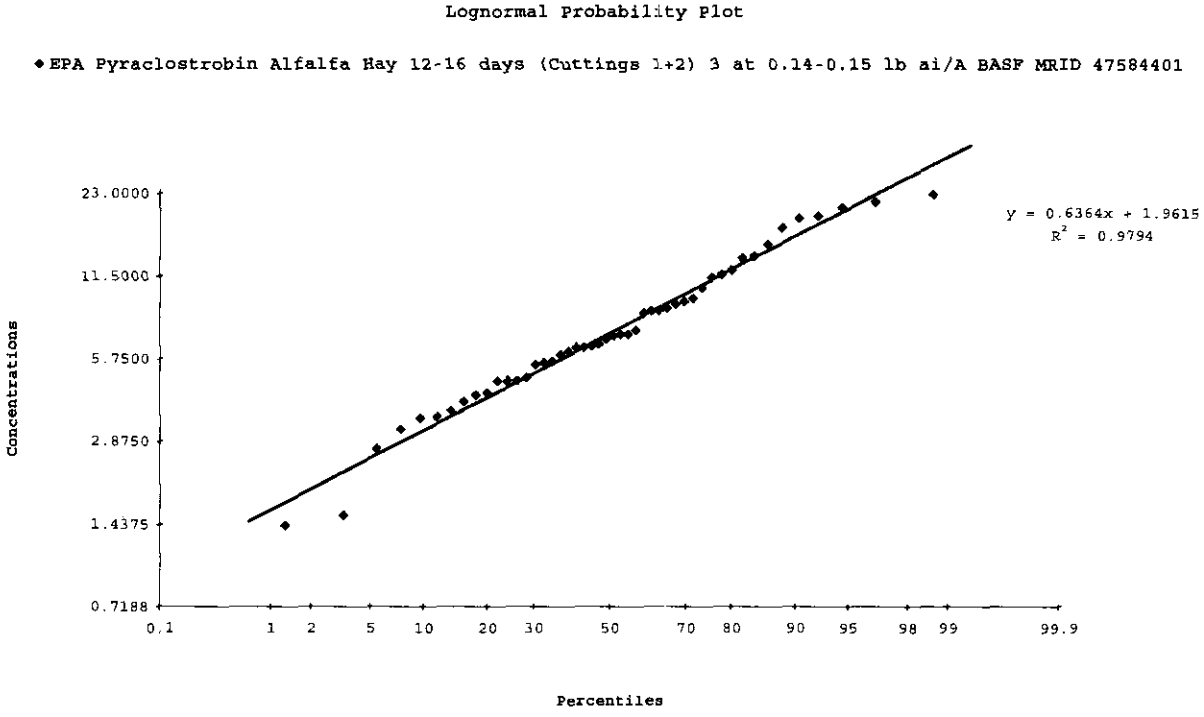


Figure II-4. Data Summary Sheet for Combined Pyraclostrobin Residues in/on Alfalfa Hay Following Three Foliar Applications Totaling ~0.44 lb ai/A.

Regulator:	EPA
Chemical:	Pyraclostrobin
Crop:	Alfalfa Hay
PHI:	16 days (Cuttings 1+2)
App. Rate:	at 0.14-0.15 lb ai/A
Submitter:	BASF
MRID Citation:	MRID 47584401
n:	48
min:	1.42
max:	22.87
median:	6.89
average:	8.56

	95th Percentile	99th Percentile	99.9th Percentile
EU Method I Normal	18 (20)	25 (25)	30 (--)
EU Method I Log Normal	25	**35** (45)	50 (--)
EU Method II Distribution-Free		25	
California Method μ + 3σ		**25**	
UPLMedian95th		**40**	
Approximate Shapiro-Francia Normality Test		0.9794 p-value > 0.05 : Do not reject lognormality assumption	

Pyraclostrobin/BAS 500 F/099100/BASF Crop Protection
DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial/Residue Decline - Alfalfa

Primary Evaluator	Dynamac Corp.	Date: 10/29/09
Approved by	W. Cutchin Chemist, RD/ARIA	

This DER was originally prepared under contract by Dynamac Corporation and has been reviewed and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT:

MRID 47584401. Jordan, J. (2008) Magnitude of Pyraclostrobin and Boscalid Residues in Seedling Alfalfa Following Applications of Pristine Fungicide. Lab Project Number: 278761, 2008/7005483. Unpublished study prepared by BASF. 383 pages.

EXECUTIVE SUMMARY:

BASF submitted field trial data for pyraclostrobin from 12 alfalfa field trials conducted in the United States in Zones 1, 2, 5, 7, 9, 10, and 11 and Canada in Zones 5 and 5B during the 2007 growing season. Each test site included one control plot and four treated plots (Treatments #2-5) that varied the number of pyraclostrobin applications (2 or 3) and the treatment to harvest intervals (14 or 21 days). For Treatments #2 and #3, a water dispersible granular (WDG) formulation containing 12.8% pyraclostrobin was applied to alfalfa as three broadcast foliar applications during vegetative development at rates of 0.142-0.161 lb ai/A, for total rates of 0.44-0.47 lb ai/A. For Treatment #2, the targeted timings for the three applications were 28 and 14 days before the 1st cutting and 14 days before the 2nd cutting. For Treatment #3, the targeted timings for the three applications were 35 and 21 days before the 1st cutting and 21 days before the 2nd cutting. The two retreatment intervals (RTIs) were 12-15 days and 28-53 days for Treatment #2 and 13-14 days and 29-53 days for Treatment #3. For Treatments #4 and #5, pyraclostrobin (12.8% WDG) was applied to alfalfa as two broadcast foliar applications during vegetative development at rates of 0.141-0.163 lb ai/A and RTIs of 28-53 days, for total rates of 0.29-0.31 lb ai/A. The targeted timings for the two applications were 14 days before the 1st and 2nd cuttings for Treatment #4 and 21 days before the 1st and 2nd cuttings for Treatment #5. All applications were made using ground equipment at volumes of 20-34 gal/A, and included the use of adjuvants.

With the exception of one test site, three cuttings of alfalfa were harvested from each plot according to typical agricultural practices, with the 3rd cutting being made at normal maturity (beginning bloom stage). The exact treatment-to-harvest intervals for each cutting are presented below along with the residue levels in forage and hay. At each cutting, single control and duplicate treated samples of alfalfa forage and hay were collected from each test, with hay samples being field-dried to a moisture content of ~10-20% prior to sampling. After sampling,

forage and hay samples were held in frozen (<-5°C) storage for up to 13 months prior to exaction for analysis. This duration is supported by the available storage stability data.

Samples of alfalfa forage and hay were analyzed for residues of pyraclostrobin and its desmethoxy metabolite BF 500-3 using a liquid chromatography with tandem mass spectroscopy /mass spectroscopy detector (LC/MS/MS) method (BASF Method D9908), which was adequately validated for data collection, based on acceptable concurrent method recoveries. The limit of quantitation (LOQ) was 0.02 ppm for each analyte in alfalfa forage and hay, and the reported limit of detection (LOD) was 0.004 ppm. Residues of metabolite BF 500-3 are expressed in parent equivalents, and the combined LOQ for alfalfa is 0.04 ppm

For Treatment #2 (3 applications each at ~0.15 lb ai/A with ~14-day PHI), combined residues of pyraclostrobin and BF 500-3 in/on forage were 0.44-7.24 ppm at 12-15 days after the second application (1st cutting), 0.85-8.15 ppm at 12-16 days after the third application (2nd cutting), and <0.04-0.24 ppm at 43-73 days after the third application (3rd cutting). Combined residues in/on hay were 1.42-20.49 ppm at 12-15 days after the second application (1st cutting), 4.02-22.87 ppm at 12-16 days after the third application (2nd cutting), and 0.05-0.87 ppm at 43-73 days after the third application (3rd cutting). For the 1st, 2nd, and 3rd cuttings, combined residues respectively averaged 2.99, 2.69 and 0.09 ppm in/on forage and 7.84, 9.28 and 0.27 ppm in/on hay.

For Treatment #3 (3 applications each at ~0.15 lb ai/A with ~21-day PHI), combined residues in/on forage were 0.06-3.38 ppm at 19-23 days after the second application (1st cutting), 0.30-2.59 ppm at 20-23 days after the third application (2nd cutting), and <0.04-0.18 ppm at 49-76 days after the third application (3rd cutting). Combined residues in/on hay were 0.08-18.75 ppm at 19-23 days after the second application (1st cutting), 1.31-8.01 ppm at 20-23 days after the third application (2nd cutting), and <0.04-0.59 ppm at 49-76 days after the third application (3rd cutting). For the 1st, 2nd, and 3rd cuttings, combined pyraclostrobin residues respectively averaged 0.89, 1.15 and 0.08 ppm in/on forage and 3.44, 3.57 and 0.20 ppm in/on hay.

For Treatment #4 (2 applications each at ~0.15 lb ai/A with ~14-day PHI), combined pyraclostrobin residues in/on forage were 0.40-5.94 ppm at 12-15 days after the first application (1st cutting), 0.57-6.56 ppm at 12-16 days after the second application (2nd cutting), and <0.04-0.18 ppm at 43-70 days after the second application (3rd cutting). Combined residues in/on hay were 1.28-15.83 ppm at 12-15 days after the first application (1st cutting), 2.77-18.81 ppm at 12-16 days after the second application (2nd cutting), and 0.05-0.46 ppm at 43-70 days after the second application (3rd cutting). For the 1st, 2nd, and 3rd cuttings, combined residues respectively averaged 2.31, 2.65 and 0.08 ppm in/on forage and 7.44, 8.59 and 0.18 ppm in/on hay.

For Treatment #5 (2 applications each at ~0.15 lb ai/A with ~21-day PHI), combined residues in/on forage were <0.04-3.03 ppm at 19-23 days after the first application (1st cutting), 0.23-2.87 ppm at 20-23 days after the second application (2nd cutting), and <0.04-0.20 ppm at 49-76 days after the second application (3rd cutting). Combined residues in/on hay were 0.20-10.48 ppm at 19-23 days after the first application (1st cutting), 1.47-12.21 ppm at 20-23 days after the second application (2nd cutting), and <0.04-0.56 ppm at 46-76 days after the second application (3rd

cutting). For the 1st, 2nd, and 3rd cuttings, combined pyraclostrobin residues respectively averaged 0.80, 1.12 and 0.08 ppm in/on forage and 2.61, 3.90 and 0.20 ppm in/on hay.

Overall, combined pyraclostrobin residues were higher in forage and hay from the treatments using 3 applications rather than 2 applications, and the residues were higher in forage and hay from treatments having the ~14-day PHI rather than the ~21-day PHI. The worse-case treatment was Treatment #2, and the highest residues in forage and hay were found in the 1st and 2nd cuttings. For Treatment #2, average combined residues from the 1st and 2nd cuttings were 2.99 and 2.69 ppm for forage and 7.84 and 9.28 ppm for hay.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the alfalfa field trial data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP# 367409.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an adverse impact on the validity of the study.

A. BACKGROUND INFORMATION

Pyraclostrobin belongs to the strobilurin class of fungicides, which are synthetic analogs of a natural antifungal substance that inhibits spore germination and mycelial growth and sporulation of the fungus on the leaf surface. The chemical structure and nomenclature of pyraclostrobin and its regulated metabolite are presented in Table A.1. The physicochemical properties of the technical grade of pyraclostrobin are presented in Table A.2.

TABLE A.1. Nomenclature of Pyraclostrobin and its Desmethoxy Metabolite.

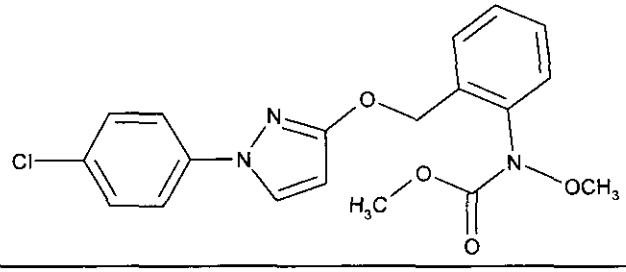
Compound	
Common name	Pyraclostrobin
Company experimental name	BAS 500 F
Molecule weight	387.8
IUPAC name	methyl *N*-{2-[1-(4-chlorophenyl)-1*H*-pyrazol-3-yloxymethyl]phenyl}(*N*-methoxy) carbamate
CAS name	methyl [2-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS registry number	175013-18-0
End-use product (EPs)	12.8% WDG (Pristine® Fungicide; EPA Reg. No. 7969-199; also contains 25.2% boscalid) 2.09 lb/gal EC (Headline® Fungicide; EPA Reg. No. 7969-186)

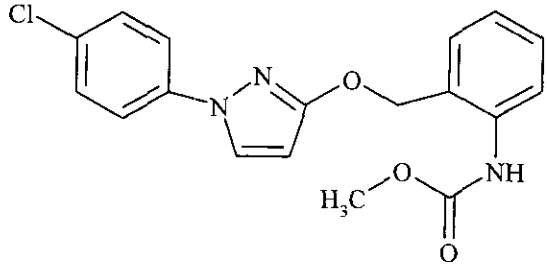
TABLE A.1. Nomenclature of Pyraclostrobin and its Desmethoxy Metabolite.	
Regulated metabolite	
Common name	pyraclostrobin desmethoxy metabolite
Company experimental name	BF 500-3
Molecular weight	357.8
Chemical name	Methyl-N-[[[1-(4-chlorophenyl) pyrazol-3-yl]oxy]o-tolyl] carbamate

TABLE A.2. Physicochemical Properties of Technical Grade Pyraclostrobin.					
Parameter	Value				References [1]
Melting point/range	63.7-65.2°C				D269848 & D274191
pH	Not reported				D269848 & D274191
Density	1.285 g/cm^3 at 20°C				D269848 & D274191
Water solubility at 20°C	2.41 mg/L (deionized water) 1.9 mg/L (pH 7) 2.3 mg/L (pH 4) 1.9 mg/L (pH 9)				D269848 & D274191
Solvent solubility (g/100 mL at 20°C)	acetone	16-20	ethyl acetate	6.7-8.0	D269848 & D274191
	methanol	4-5	2-propanol	<0.01	
	acetonitrile	4-5	dichloromethane	20-25	
	toluene	2-5	n-heptane	<0.01	
	1-octanol	<0.01	olive oil	2.9	
	N,N-DMF >25				
Vapor pressure	2.6 x 10^{-10} hPa at 20EC 6.4 x 10^{-10} hPa at 25°C				D269848 & D274191
Dissociation constant, pK_a	Does not dissociate in water.				D269848 & D274191
Octanol/water partition coefficient, Log(K_{OW}) at room temperature	3.80 at pH 6.2 4.18 at pH 6.5				D269848 & D274191
UV/visible absorption spectrum	λ_{max} = 275 nm				D269848

[1] Product Chemistry data were reviewed by the Registration Division (DP#s 269848 and D274191, 5/3/2001, 5/15/2001, and 6/7/2001, S. Malak).

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

A total of 12 alfalfa field trials were conducted in the United States in Zones 1, 2, 5, 7, 9, 10, and 11 and Canada in Zones 5B and 5 during the 2007 growing season (Tables B.1.1 and B.1.3). Each test site included one control plot and four treated plots (Treatments #2-5), which varied the number of pyraclostrobin applications (2 or 3) and the treatment to harvest intervals (14 or 21 days). For Treatments #2 and #3, pyraclostrobin (12.8% WDG) was applied to alfalfa as three broadcast foliar applications during vegetative development at rates of 0.142-0.161 lb ai/A, for total rates of 0.44-0.47 lb ai/A (Table B.1.2). For Treatment #2, the targeted timings for the three applications were 28 and 14 days before the 1st cutting and 14 days before the 2nd cutting. For Treatment #3, the targeted timings for the three applications were 35 and 21 days before the

1st cutting and 21 days before the 2nd cutting. The RTIs were 12-15 days and 28-53 days for Treatment #2 and 13-14 days and 29-53 days for Treatment #3.

For Treatments #4 and #5, pyraclostrobin (12.8% WDG) was applied to alfalfa as two broadcast foliar applications during vegetative development at rates of 0.141-0.163 lb ai/A and RTIs of 28-53 days, for total rates of 0.29-0.31 lb ai/A. The targeted timings for the two applications 14 days before the 1st and 2nd cuttings for Treatment #4 and 21 days before the 1st and 2nd cuttings for Treatment #5.

All applications were made using ground equipment at volumes of 20-34 gal/A, and included the use of adjuvants (rates not reported).

Weather conditions were considered normal for most test sites during the study period; some rainfall and/or temperature conditions at test sites were above or below normal. Irrigation was used to supplement precipitation as needed. There were no meteorological abnormalities that occurred during the conduct of the study. Information on maintenance pesticides and fertilizers was also provided for each site.

TABLE B.1.1. Trial Site Conditions.

Trial Identification (City, State; Year)/ Trial ID No.	Soil characteristics			
	Type	%OM	pH	CEC (meq/g)
Lehigh, PA; 2007 RCN R070118	Loam	NR	NR	NR
Louisa, VA; 2007 RCN R070119	Sandy loam	NR	NR	NR
Cass, ND; 2007 RCN R070120	Clay loam	NR	NR	NR
Verchères, QB Canada; 2007 RCN R070121	Clay	NR	NR	NR
Jefferson, IA; 2007 RCN R070122	Silty clay loam	NR	NR	NR
Portage La Prairie, MB Canada; 2007 RCN R070123	Clay loam	NR	NR	NR
Pepin, WI; 2007 RCN R070124	Sandy loam	NR	NR	NR
Freeborn, MN; 2007 RCN R070125	Loam	NR	NR	NR
Stutsman, ND; 2007 RCN R070126	Loam	NR	NR	NR
Cache, UT; 2007 RCN R070127	Silty clay	NR	NR	NR
Stanislaus, CA; 2007 RCN R070128	Sandy loam	NR	NR	NR
Power, ID; 2007 RCN R070129	Silty loam	NR	NR	NR

TABLE B.1.2. Study Use Pattern for Pyraclostrobin.

Location (City, State/Province; Year) Trial ID	End-use Product	Trt. No.	Application Information					Tank Mix/ Adjuvants
			Method; Timing	Volume (GPA)	Single Rate (lb ai/A)	RTI [1] (days)	Total Rate (lb ai/A)	
Lehigh, PA; 2007 RCN R070118	12.8% WDG	2	Three broadcast foliar applications during pre-bloom	31-33	0.152-0.154	14, 36	0.46	Dyne-Amic
		3	Three broadcast foliar applications from early seedling to pre-bloom	33-34	0.150-0.154	13, 36	0.46	Dyne-Amic
		4	Two broadcast foliar applications during pre-bloom	34	0.154	36	0.31	Dyne-Amic
		5	Two broadcast foliar applications during pre-bloom	33	0.152-0.154	36	0.31	Dyne-Amic
Louisa, VA; 2007 RCN R070119	12.8% WDG	2	Three broadcast foliar applications at BBCH 35, 43, and 37	22	0.150-0.151	14, 53	0.45	LESCO
		3	Three broadcast foliar applications at BBCH 33, 35, and 40	22-23	0.149-0.154	14, 53	0.45	LESCO
		4	Two broadcast foliar applications at BBCH 45	22	0.149-0.150	53	0.30	LESCO
		5	Two broadcast foliar applications at BBCH 43	22	0.148-0.150	53	0.30	LESCO
Cass, ND; 2007 RCN R070120	12.8% WDG	2	Three broadcast foliar applications during mid-vegetative growth and 10% flower	25-26	0.150-0.154	14, 34	0.46	Activator 90
		3	Three broadcast foliar applications during mid-vegetative growth and 5% flower	25-27	0.152-0.161	14, 34	0.47	Activator 90
		4	Two broadcast foliar applications during 10% flower and mid-vegetative growth	25	0.150-0.151	34	0.30	Activator 90
		5	Two broadcast foliar applications during 5% flower and mid-vegetative growth	25	0.150-0.151	34	0.30	Activator 90
Verchères, QB Canada; 2007 RCN R070121	12.8% WDG	2	Three broadcast foliar applications from 8-10 leaves to early bloom	28-30	0.142-0.152	12, 41	0.44	Agsurf
		3	Three broadcast foliar applications from 5-6 leaves to early bloom	29-31	0.148-0.157	13, 41	0.46	Agsurf
		4	Two broadcast foliar applications during early bloom	30	0.151-0.152	41	0.30	Agsurf
		5	Two broadcast foliar applications during early bloom	29-30	0.148-0.152	41	0.30	Agsurf
Jefferson, IA; 2007 RCN R070122	12.8% WDG	2	Three broadcast foliar applications from 4-5 to 10 trifoliate leaves	25-27	0.149-0.150	13, 42	0.45	Agri-Dex
		3	Three broadcast foliar applications from 2 to 5 trifoliate leaves	24-25	0.149-0.150	14, 42	0.45	Agri-Dex
		4	Two broadcast foliar applications from 7 to 10 trifoliate leaves	25	0.149-0.150	42	0.30	Agri-Dex
		5	Two broadcast foliar applications at 5 trifoliate leaves	24-25	0.147-0.150	42	0.30	Agri-Dex
Portage La Prairie, MB Canada; 2007 RCN R070123	12.8% WDG	2	Three broadcast foliar applications from early vegetative growth to BBCH 30	26-27	0.147-0.151	14, 40	0.45	Merge
		3	Three broadcast foliar applications from early vegetative growth to BBCH 19	26-27	0.142-0.147	14, 41	0.44	Merge
		4	Two broadcast foliar applications from early vegetative growth to BBCH 30	27	0.148-0.151	40	0.30	Merge
		5	Two broadcast foliar applications from mid-vegetative growth to BBCH 19	26-27	0.141-0.147	41	0.29	Merge

TABLE B.1.2. Study Use Pattern for Pyraclostrobin.

Location (City, State/Province; Year) Trial ID	End-use Product	Trt. No.	Application Information					Tank Mix/ Adjuvants
			Method; Timing	Volume (GPA)	Single Rate (lb ai/A)	RTI [1] (days)	Total Rate (lb ai/A)	
Pepin, WI; 2007 RCN R070124	12.8% WDG	2	Three broadcast foliar applications from pre-bloom to 12 in. regrowth	25	0.150	13, 29	0.45	Dyne-Amic
		3	Three broadcast foliar applications during 2-4 in. regrowth	25	0.150-0.152	13, 29	0.45	Dyne-Amic
		4	Two broadcast foliar applications from pre-bloom to 12 in. regrowth	25	0.148-0.152	29	0.30	Dyne-Amic
		5	Two broadcast foliar applications from pre-bloom to 4 in. regrowth	25-26	0.150-0.152	29	0.30	Dyne-Amic
Freeborn, MN; 2007 RCN R070125	12.8% WDG	2	Three broadcast foliar applications from 6-9 in. to vegetative growth	21-23	0.151-0.152	13, 42	0.46	Preference
		3	Three broadcast foliar applications 4-8 in. to vegetative growth	20-21	0.147-0.150	14, 42	0.45	Preference
		4	Two broadcast foliar applications during vegetative growth	21-23	0.150-0.152	42	0.30	Preference
		5	Two broadcast foliar applications during vegetative growth	21	0.150-0.152	42	0.30	Preference
Stutsman, ND; 2007 RCN R070126	12.8% WDG	2	Three broadcast foliar applications during mid-vegetative growth and 5% flowering	25	0.148-0.152	14, 36	0.45	Activator 90
		3	Three broadcast foliar applications from BBCH 29 to mid-vegetative growth	25-26	0.148-0.156	14, 35	0.46	Activator 90
		4	Two broadcast foliar applications from 5% flowering to mid-vegetative growth	25-26	0.152-0.153	36	0.31	Activator 90
		5	Two broadcast foliar applications during mid-vegetative growth	25	0.150-0.152	35	0.30	Activator 90
Cache, UT; 2007 RCN R070127	12.8% WDG	2	Three broadcast foliar applications from 3-5 in. to vegetative growth	22	0.151-0.160	14, 34	0.47	Agral 90
		3	Three broadcast foliar applications from 3-5 trifoliate to vegetative growth	20-22	0.153-0.158	14, 34	0.46	Agral 90
		4	Two broadcast foliar applications during vegetative growth	20-22	0.148-0.152	34	0.30	Agral 90
		5	Two broadcast foliar applications during vegetative growth	21-23	0.151-0.163	34	0.31	Agral 90
Stanislaus, CA; 2007 RCN R070128	12.8% WDG	2	Three broadcast foliar applications during BBCH 37, 38, and 35	25	0.147-0.149	15, 28	0.45	Silwet L-77
		3	Three broadcast foliar applications during BBCH 35, 36, and 33	25	0.148-0.151	13, 32	0.45	Silwet L-77
		4	Two broadcast foliar applications during BBCH 38 and 35	25	0.148-0.150	28	0.30	Silwet L-77
		5	Two broadcast foliar applications during BBCH 36 and 33	25	0.148-0.149	32	0.30	Silwet L-77
Power, ID; 2007 RCN R070129	12.8% WDG	2	Three broadcast foliar applications from 4-6 trifoliate leaves to vegetative growth	22-23	0.152-0.157	15, 40	0.46	Agral 90
		3	Three broadcast foliar applications 4-5 trifoliate leaves to vegetative regrowth	21-23	0.151-0.158	13, 41	0.46	Agral 90
		4	Two broadcast foliar applications during vegetative growth	22	0.151-0.152	40	0.30	Agral 90
		5	Two broadcast foliar applications during vegetative growth and regrowth	21-22	0.151-0.153	41	0.30	Agral 90

[1] RTI = Retreatment Interval

[2] The rates for the adjuvants were not reported.

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Zones	Alfalfa		
	Submitted	Requested [1]	
		Canada	U.S.
1	1	--	1
1A	--	--	--
2	1	--	1
3	--	--	--
4	--	--	--
5	5	--	6
5A	--	--	--
5B	1	--	--
6	--	--	--
7	1	--	1
7A	--	--	--
8	--	--	--
9	1	--	1
10	1	--	1
11	1	--	1
12	--	--	--
13	--	--	--
14	--	--	--
Total	12	NA	12

[1] Regions 14-21 were not included as the proposed use is for the US only. Two trials (region 5 and 5B) were conducted in Canada.
NA = not applicable.

B.2. Sample Handling and Preparation

With the exception of one test site, three cuttings of alfalfa were harvested from each plot according to the typical agricultural practices for each region, with the 3rd cutting being made at normal maturity (beginning bloom stage). At one of the Canadian sites (Trial# R070123), a 3rd cutting was not harvested due to cooler weather that resulted in slower crop development after the 2nd cutting.

For Treatment #2, the 1st cutting was made 12-15 days after the 2nd application, the 2nd cutting was made 12-16 days after the 3rd application, and the 3rd cutting was made 43-73 days after the 3rd application. For Treatment #3, the 1st cutting was made 19-23 days after the 2nd application, the 2nd cutting was made 20-23 days after the 3rd application, and the 3rd cutting was made 49-76 days after the 3rd application. For Treatment #4, the 1st cutting was made 12-15 days after the 1st application, the 2nd cutting was made 12-16 days after the 2nd application, and the 3rd cutting was made 43-70 days after the 2nd application. For Treatment #5, the 1st cutting was made 19-23 days after the 1st application, the 2nd cutting was made 20-23 days after the 2nd application, and the 3rd cutting was made 49-76 days after the 2nd application.

At each cutting, single control and duplicate treated samples of alfalfa forage (≥2.2 lb/sample) and hay (≥1.1 lb/sample) were collected from each test. Prior to collection, hay samples were field-dried for 2-19 days to a moisture content of ~10-20%, with the exception of one field trial (Trial #R070123) where hay samples were field dried for 12-39 days. All samples were placed in frozen storage at the field sites (time not specified) and stored frozen at the field sites for 0-198 days. Samples were then shipped by ACDS freezer truck to the analytical laboratory, BASF Agricultural Products Center (APC), Research Triangle Park, NC, and stored frozen (≤-5EC) prior to analysis. Moisture content was determined for selected forage and hay samples. Moisture contents were 31-88% in for forage samples and 12-54% for hay samples.

B.3. Analytical Methodology

Samples of alfalfa forage and hay were analyzed for residues of pyraclostrobin and Metabolite BF 500-3 using an LC/MS/MS method (BASF Method D9908) entitled "Method for Determining BAS 500F, BF 500-3, and BAS 510F Residues in Plant Matrices using LC/MS/MS." This method is one of the proposed tolerance enforcement methods for plant commodities, which was forwarded to ACB/BEAD for an Agency method validation (DP# 269850, L. Cheng, 11/8/2000).

For this method, residues were extracted from forage and hay with methanol:water:2 N HCl (70:25:5; v/v/v) and centrifuged. Residues were then diluted with 1N HCl saturated with NaCl, and partitioned into cyclohexane. Residues were concentrated to dryness, re-dissolved in methanol:water:4 mM ammonium formate (80:20:0.1, v/v/v), and analyzed by LC/MS/MS using external calibration curves. Residue were detected and quantified by monitoring the *m/z* 388→194 transition for pyraclostrobin and the *m/z* 358→164 transition for BF 500-3. The validated LOQ was 0.02 ppm for each analyte, and the LOD was 0.004 ppm.

The above method was validated in conjunction with the analysis of field trial samples. Control samples of alfalfa forage and hay were fortified with pyraclostrobin and metabolite BF 500-3 at 0.02 and 50.0 ppm.

C. RESULTS AND DISCUSSION

The LC/MS/MS method (BASF Method D9908) used for determining residues of pyraclostrobin and BF 500-3 in/on alfalfa forage and hay was adequately validated in conjunction with the analysis of field trial samples. For pyraclostrobin, the average concurrent validation recoveries (±S.D.) were 94 ± 12% for forage and 87 ± 10% for hay. For BF 500-3, the average concurrent validation recoveries (±S.D.) were 91 ± 13% for forage and 84 ± 10% for hay. Apparent residues of pyraclostrobin and BF 500-3 were <LOQ (<0.02 ppm) in/on control samples of alfalfa forage and hay, with a few exceptions. One control hay sample had apparent pyraclostrobin residues of 0.055-0.065 ppm, and another control hay sample had apparent residues of pyraclostrobin and BF 500-3 at 0.022-0.023 ppm (however, subsequent analyses indicated residues were <LOQ in this control sample). Adequate sample calculations and example chromatograms were provided, and the fortification levels used for the concurrent recoveries were similar in magnitude to the measured residue levels.

Alfalfa forage and hay samples were stored at ≤-5°C for up to 13 months prior to analysis (Table C.2). Adequate storage stability data are available indicating that pyraclostrobin and metabolite BF 500-3 are stable under frozen storage conditions for at least 25 months in various crop matrices, including sugar beet top and wheat grain and straw (DP# 269668, L. Cheng, 11/28/01). These data will support the sample storage conditions and durations for the current alfalfa field trials.

The combined residues of pyraclostrobin and BF 500-3 in/on the 22-24 samples of forage and hay from each treatment and each harvest interval are presented in Table C.3 and summarized in Table C.4. For Treatment #2 (3 applications each at ~0.15 lb ai/A with ~14-day PHI), combined residues in/on forage were 0.44-7.24 ppm at 12-15 days after the second application (1st cutting), 0.85-8.15 ppm at 12-16 days after the third application (2nd cutting), and <0.04-0.24 ppm at 43-73 days after the third application (3rd cutting). Combined residues in/on hay were 1.42-20.49 ppm at 12-15 days after the second application (1st cutting), 4.02-22.87 ppm at 12-16 days after the third application (2nd cutting), and 0.05-0.87 ppm at 43-73 days after the third application (3rd cutting). For the 1st, 2nd, and 3rd cuttings, combined residues respectively averaged 2.99, 2.69 and 0.09 ppm in/on forage and 7.84, 9.28 and 0.27 ppm in/on hay.

For Treatment #3 (3 applications each at ~0.15 lb ai/A with ~21-day PHI), combined residues in/on forage were 0.06-3.38 ppm at 19-23 days after the second application (1st cutting), 0.30-2.59 ppm at 20-23 days after the third application (2nd cutting), and <0.04-0.18 ppm at 49-76 days after the third application (3rd cutting). Combined residues in/on hay were 0.08-18.75 ppm at 19-23 days after the second application (1st cutting), 1.31-8.01 ppm at 20-23 days after the third application (2nd cutting), and <0.04-0.59 ppm at 49-76 days after the third application (3rd cutting). For the 1st, 2nd, and 3rd cuttings, combined pyraclostrobin residues respectively averaged 0.89, 1.15 and 0.08 ppm in/on forage and 3.44, 3.57 and 0.20 ppm in/on hay.
For Treatment #4 (2 applications each at ~0.15 lb ai/A with ~14-day PHI), combined pyraclostrobin residues in/on forage were 0.40-5.94 ppm at 12-15 days after the first application (1st cutting), 0.57-6.56 ppm at 12-16 days after the second application (2nd cutting), and <0.04-0.18 ppm at 43-70 days after the second application (3rd cutting). Combined residues in/on hay were 1.28-15.83 ppm at 12-15 days after the first application (1st cutting), 2.77-18.81 ppm at 12-16 days after the second application (2nd cutting), and 0.05-0.46 ppm at 43-70 days after the second application (3rd cutting). For the 1st, 2nd, and 3rd cuttings, combined residues respectively averaged 2.31, 2.65 and 0.08 ppm in/on forage and 7.44, 8.59 and 0.18 ppm in/on hay.

For Treatment #5 (2 applications each at ~0.15 lb ai/A with ~21-day PHI), combined residues in/on forage were <0.04-3.03 ppm at 19-23 days after the first application (1st cutting), 0.23-2.87 ppm at 20-23 days after the second application (2nd cutting), and <0.04-0.20 ppm at 49-76 days after the second application (3rd cutting). Combined residues in/on hay were 0.20-10.48 ppm at 19-23 days after the first application (1st cutting), 1.47-12.21 ppm at 20-23 days after the second application (2nd cutting), and <0.04-0.56 ppm at 46-76 days after the second application (3rd cutting). For the 1st, 2nd, and 3rd cuttings, combined pyraclostrobin residues respectively averaged 0.80, 1.12 and 0.08 ppm in/on forage and 2.61, 3.90 and 0.20 ppm in/on hay.

Overall, combined pyraclostrobin residues were higher in forage and hay from the treatments using 3 applications rather than 2 applications, and the residues were higher in forage and hay from treatments having the ~14-day PHI rather than the ~21-day PHI. The worse-case treatment was Treatment #2, and the highest residues in forage and hay were found in the 1st and 2nd cuttings. For Treatment #2, average combined residues from the 1st and 2nd cuttings were 2.99 and 2.69 ppm for forage and 7.84 and 9.28 ppm for hay. Based on the residue data from the two harvest intervals (14 vs. 21 days), combined pyraclostrobin residues were shown to decline at the longer post-treatment interval.

Common cultural practices were used to maintain plants, and the weather conditions and the maintenance chemicals and fertilizer used in the study did not have a notable impact on the residue data.

TABLE C.1. Summary of Concurrent Recoveries of Pyraclostrobin and Metabolite BF 500-3 from Alfalfa.

Matrix	Spike Level (ppm)	Sample Size (n)	Recoveries (%)	Mean ± Std. Dev. (%)
Pyraclostrobin				
Forage	0.02	15	85, 84, 84, 85, 87, 105, 133, 109, 82, 99, 91, 103, 114, 113, 90	98 ± 15
	50.0	15	100, 88, 93, 92, 96, 93, 87, 84, 73, 92, 86, 98, 92, 93, 85	90 ± 7
	Combined	**30**	**73-133**	**94 ± 12**
Hay	0.02	14	87, 108, 78, 83, 87, 72, 90, 102, 91, 74, 115, 80, 90, 82	89 ± 12
	50.0	15	78, 94, 76, 79, 79, 83, 89, 85, 90, 88, 94, 84, 89, 87, 75	85 ± 6
	Combined	**29**	**72-115**	**87 ± 10**
BF 500-3				
Forage	0.02	15	82, 80, 93, 96, 86, 80, 92, 129, 108, 76, 86, 107, 111, 117, 90	96 ± 16
	50.0	15	93, 84, 93, 93, 89, 95, 81, 71, 85, 66, 80, 98, 84, 97, 83	86 ± 9
	Combined	**30**	**66-129**	**91 ± 13**
Hay	0.02	13	84, 76, 74, 85, 78, 91, 107, 94, 79, 83, 81, 109, 84	87 ± 11
	50.0	14	92, 97, 73, 75, 70, 84, 83, 86, 82, 90, 82, 88, 84, 69	83 ± 8
	Combined	**27**	**69-109**	**84 ± 10**

TABLE C.2. Summary of Storage Conditions.

Matrix	Storage Temperature (°C)	Actual Storage Duration (months) [1]	Interval of Demonstrated Storage Stability (months) [2]
Alfalfa Forage	<-5	5-13	25
Alfalfa Hay			

[1] Interval from harvest to extraction for analysis. Samples were stored up to 8 days prior to analysis.

[2] Storage stability data are available indicating that pyraclostrobin and metabolite BF 500-3 are stable for at least 25 months in various crop matrices, including sugar beet tops and wheat straw (DP# 269668, L. Cheng, 11/28/2001).

TABLE C.3. Residue Data from Alfalfa Field Trials with Pyraclostrobin (WDG).

Trial ID (City, State; Year)	Zone	Variety	Total Rate (lb ai/A)	Trt. [1] No.	Matrix	Cutting	PHI (days)	Residues (ppm) [2]					
								Pyraclostrobin		B 500-3		Combined [3]	
Lehigh, PA; 2007 RCN R070118	1	Ameristand 403T	0.46	2	Forage	1	15	2.00	1.71	**0.27**	**0.25**	2.27	1.96
						2	16	**4.59**	4.65	0.78	0.78	5.37	5.43
						3	47-48	0.02	(0.014)	(0.007)	(0.005)	0.04	0.04
					Hay	1	15	5.50	5.21	0.83	0.75	6.33	5.96
						2	16	13.03	11.63	**1.97**	2.00	15	13.63
						3	47-48	0.05	0.06	(0.011)	(0.011)	0.07	0.08
			0.46	3	Forage	1	22	0.64	0.75	**0.14**	**0.15**	0.78	0.9
						2	23	1.91	1.90	**0.30**	**0.31**	2.21	2.21
						3	54	(0.019)	(0.017)	(0.006)	(0.006)	0.04	0.04
					Hay	1	22	1.91	1.87	**0.36**	**0.36**	2.27	2.23
						2	23	4.19	4.58	**0.62**	**0.70**	4.81	5.28
						3	54	0.02	0.02	(0.006)	(0.006)	0.04	0.04
			0.31	4	Forage	1	15	1.99	1.76	**0.21**	**0.22**	2.2	1.98
						2	16	**4.59**	**4.80**	0.72	0.77	5.31	5.57
						3	47	(0.019)	0.02	(0.007)	(0.008)	0.04	0.04
					Hay	1	15	5.34	5.51	**0.55**	**0.60**	5.89	6.11
						2	16	13.18	12.53	1.95	**1.86**	15.13	14.39
						3	47	0.07	0.06	(0.015)	(0.013)	0.09	0.08
			0.31	5	Forage	1	22	**0.49**	0.56	**0.09**	**0.10**	0.58	0.66
						2	23	1.36	1.02	**0.19**	**0.16**	1.55	1.18
						3	54	(0.010)	(0.008)	ND	ND	0.04	0.04
					Hay	1	22	1.70	1.49	**0.24**	**0.21**	1.94	1.7
						2	23	3.32	3.43	**0.44**	**0.45**	3.76	3.88
						3	54	0.03	0.04	(0.006)	(0.007)	0.05	0.06
Louisa, VA; 2007 RCN R070119	2	Starbuck	0.45	2	Forage	1	14	5.39	6.37	0.74	0.87	6.13	7.24
						2	14	5.93	7.29	0.74	0.86	6.67	8.15
						3	47-70	**0.03**	**0.17**	**(0.009)**	**0.04**	0.05	0.21
					Hay	1	14	10.13	11.77	1.49	1.62	11.62	13.39
						2	14	20.42	19.23	**2.45**	**2.27**	22.87	21.5
						3	47-70	**0.03**	**0.04**	**(0.012)**	**(0.013)**	0.05	0.06
			0.45	3	Forage	1	21	0.17	0.18	0.04	0.04	0.21	0.22
						2	21	0.61	0.63	0.08	0.08	0.69	0.71
						3	55	(0.003)	(0.004)	(0.003)	(0.004)	0.04	0.04
					Hay	1	21	0.13	0.06	(0.018)	(0.010)	0.15	0.08
						2	21	1.45	2.06	0.15	**0.23**	1.6	2.29
						3	55	0.03	0.04	(0.011)	(0.012)	0.05	0.06

TABLE C.3. Residue Data from Alfalfa Field Trials with Pyraclostrobin (WDG).

Trial ID (City, State; Year)	Zone	Variety	Total Rate (lb ai/A)	Trt. [1] No.	Matrix	Cutting	PHI (days)	Residues (ppm) [2]					
								Pyraclostrobin		B 500-3		Combined [3]	
			0.30	4	Forage	1	14	4.04	3.37	0.32	0.29	4.36	3.66
						2	14	5.75	6.03	0.52	0.53	6.27	6.56
						3	48	**0.031**	(0.011)	(0.010)	(0.004)	0.051	0.04
					Hay	1	14	9.19	10.32	**1.01**	**1.12**	10.2	11.44
						2	14	16.89	15.28	1.92	1.77	18.81	17.05
						3	48	0.04	0.05	0.05	(0.011)	0.09	0.07
			0.30	5	Forage	1	21	(0.017)	(0.009)	(0.004)	ND	0.04	0.04
						2	21	0.64	0.87	0.08	0.10	0.72	0.97
						3	55	ND	**(0.007)**	ND	(0.006)	0.04	0.04
					Hay	1	21	**0.33**	**0.38**	0.06	0.06	0.39	0.44
						2	21	2.62	2.29	**0.31**	**0.27**	2.93	2.56
						3	55	(0.014)	(0.012)	(0.006)	(0.006)	0.04	0.04
Cass, ND; 2007 RCN R070120	5	Mycogen 4A421	0.46	2	Forage	1	12	2.11	1.76	**0.36**	**0.29**	2.47	2.05
						2	13	2.91	2.55	**0.42**	**0.40**	3.33	2.95
						3	43-54	0.07	0.06	**(0.014)**	**(0.011)**	0.09	0.08
					Hay	1	12	**2.92**	**5.68**	**0.57**	**1.11**	3.49	6.79
						2	13	8.05	7.57	1.47	1.22	9.52	8.79
						3	43-54	0.18	0.18	0.05	0.05	0.23	0.23
			0.47	3	Forage	1	19	**0.47**	0.59	**0.10**	**0.14**	0.57	0.73
						2	20	1.00	1.08	**0.19**	**0.19**	1.19	1.27
						3	54	0.04	0.04	**(0.007)**	**(0.009**	0.06	0.06
					Hay	1	19	1.27	1.44	0.24	0.27	1.51	1.71
						2	20	3.48	3.51	0.53	0.53	4.01	4.04
						3	54	0.14	0.14	0.04	0.04	0.18	0.18
			0.30	4	Forage	1	12	1.30	1.64	**0.15**	**0.19**	1.45	1.83
						2	13	2.00	2.36	**0.29**	**0.35**	2.29	2.71
						3	47	0.03	0.03	**(0.007)**	**(0.006)**	0.05	0.05
					Hay	1	12	4.80	4.96	0.49	0.49	5.29	5.45
						2	13	6.81	7.70	**1.29**	**1.35**	8.1	9.05
						3	47	0.10	0.10	0.02	0.02	0.12	0.12
			0.30	5	Forage	1	19	**0.40**	**0.28**	**0.08**	**0.05**	0.48	0.33
						2	20	0.90	0.80	**0.16**	**0.16**	1.06	0.96
						3	54	0.02	0.04	**(0.005)**	**(0.010)**	0.04	0.06
					Hay	1	19	**0.52**	**0.54**	0.09	0.10	0.61	0.64
						2	20	3.35	3.47	0.52	0.50	3.87	3.97
						3	54	0.09	0.11	0.03	0.03	0.12	0.14
Verchères, QB Canada; 2007 RCN R070121	5B	WL237	0.44	2	Forage	1	14	**0.35**	**0.40**	0.09	0.10	0.44	0.5
						2	14	1.18	1.28	0.19	0.20	1.37	1.48
						3	43-46	(0.012)	(0.013)	ND	ND	0.04	0.04
					Hay	1	14	1.26	1.16	0.29	0.26	1.55	1.42
						2	14	4.19	3.90	**0.73**	0.88	4.92	4.78
						3	43-46	0.03	0.03	(0.011)	(0.009)	0.05	0.05
			0.46	3	Forage	1	20	0.13	**0.13**	0.03	0.03	0.16	0.16
						2	20	1.07	1.16	0.24	0.25	1.31	1.41
						3	76	(0.013)	0.02	ND	(0.006)	0.04	0.04
					Hay	1	20	**0.38**	**0.37**	**0.11**	**0.10**	0.49	0.47

TABLE C.3. Residue Data from Alfalfa Field Trials with Pyraclostrobin (WDG).

Trial ID (City, State; Year)	Zone	Variety	Total Rate (lb ai/A)	Trt. [1] No.	Matrix	Cutting	PHI (days)	Residues (ppm) [2]					
								Pyraclostrobin		B 500-3		Combined [3]	
						2	20	3.73	3.47	0.81	0.83	4.54	4.3
						3	76	0.03	0.02	(0.011)	(0.008)	0.05	0.04
			0.30	4	Forage	1	14	**0.36**	**0.44**	0.08	0.10	0.44	0.54
						2	14	1.12	1.11	0.23	0.22	1.35	1.33
						3	70	(0.019)	(0.018)	(0.006)	ND	0.04	0.04
					Hay	1	14	1.06	1.19	**0.22**	**0.27**	1.28	1.46
						2	14	3.94	4.52	0.78	0.92	4.72	5.44
						3	70	0.05	0.05	(0.016)	(0.014)	0.07	0.07
			0.30	5	Forage	1	20	0.12	0.11	0.03	0.03	0.15	0.14
						2	20	1.06	1.01	0.23	0.22	1.29	1.23
						3	76	(0.019)	0.02	(0.004)	(0.004)	0.04	0.04
					Hay	1	20	**0.34**	**0.34**	**0.09**	**0.10**	0.43	0.44
						2	20	3.58	3.75	0.85	0.86	4.43	4.61
						3	76	**0.08**	**0.05**	**(0.019)**	**(0.014)**	0.1	0.07
Jefferson, IA; 2007 RCN R070122	5	MP1000	0.45	2	Forage	1	15	1.92	2.90	0.12	0.20	2.04	3.1
						2	14	1.31	1.32	0.11	0.10	1.42	1.42
						3	44-48	(0.010)	(0.017)	ND	ND	0.04	0.04
					Hay	1	15	8.69	9.96	0.38	0.48	9.07	10.44
						2	14	5.16	5.31	0.31	0.32	5.47	5.63
						3	44-48	**0.07**	**0.12**	(0.010)	(0.012)	0.09	0.14
			0.45	3	Forage	1	22	0.69	0.73	0.05	0.06	0.74	0.79
						2	21	**0.57**	0.73	0.08	0.08	0.65	0.81
						3	50	(0.011)	(0.014)	ND	ND	0.04	0.04
					Hay	1	22	1.96	2.43	0.16	0.19	2.12	2.62
						2	21	3.49	4.30	0.36	0.38	3.85	4.68
						3	50	**0.03**	**0.03**	(0.007)	(0.007)	0.05	0.05
			0.30	4	Forage	1	15	2.37	1.87	0.15	0.12	2.52	1.99
						2	14	2.18	1.62	0.15	0.13	2.33	1.75
						3	43	(0.012)	(0.014)	ND	<0.02	0.04	0.04
					Hay	1	15	6.50	6.26	0.36	0.37	6.86	6.63
						2	14	7.36	6.84	0.44	0.41	7.8	7.25
						3	43	**0.05**	**0.03**	(0.008)	(0.008)	0.07	0.05
			0.30	5	Forage	1	22	1.20	0.89	0.08	0.06	1.28	0.95
						2	21	1.37	1.29	0.14	0.13	1.51	1.42
						3	50	(0.013)	(0.004)	ND	ND	0.04	0.04
					Hay	1	22	3.43	1.43	0.25	0.11	3.68	1.54
						2	21	4.76	4.38	0.46	0.44	5.22	4.82
						3	50	**0.06**	**0.04**	(0.011)	(0.010)	0.08	0.06
Portage La Prairie, MB Canada; 2007 RCN R070123	5	Common #1	0.45	2	Forage	1	13	4.41	**3.80**	**1.04**	0.69	5.45	4.49
						2	16	**3.46**	**3.00**	0.74	0.73	4.2	3.73
					Hay	1	13	17.31	16.05	3.18	2.99	20.49	19.04
						2	16	9.78	9.19	**2.29**	**2.19**	12.07	11.38
			0.44	3	Forage	1	20	1.29	0.88	0.22	0.16	1.51	1.04
						2	22	2.26	1.97	0.33	0.38	2.59	2.35
					Hay	1	20	**4.69**	**4.80**	0.92	0.85	5.61	5.65
						2	22	6.79	6.19	**1.22**	**1.23**	8.01	7.42

TABLE C.3. Residue Data from Alfalfa Field Trials with Pyraclostrobin (WDG).

Trial ID (City, State; Year)	Zone	Variety	Total Rate (lb ai/A)	Trt. [1] No.	Matrix	Cutting	PHI (days)	Residues (ppm) [2]					
								Pyraclostrobin		B 500-3		Combined [3]	
			0.30	4	Forage	1	13	3.25	2.64	0.54	0.41	3.79	3.05
						2	16	**3.39**	**2.75**	0.73	0.63	4.12	3.38
					Hay	1	13	12.51	12.32	**2.21**	**2.10**	14.72	14.42
						2	16	9.62	8.82	2.21	**1.94**	11.83	10.76
			0.29	5	Forage	1	20	1.22	1.27	0.20	0.22	1.42	1.49
						2	22	2.53	2.40	0.34	0.29	2.87	2.69
					Hay	1	20	5.30	5.31	0.98	**1.09**	6.28	6.4
						2	22	10.74	7.86	**1.47**	**1.32**	12.21	9.18
Pepin, WI; 2007 RCN R070124	5	Garst 6415	0.45	2	Forage	1	14	**5.62**	**5.06**	**0.95**	0.66	6.57	5.72
						2	15	1.13	1.41	0.10	0.12	1.23	1.53
						3	47-49	0.06	0.06	0.02	(0.015)	0.08	0.08
					Hay	1	14	**14.99**	**8.02**	**2.30**	**0.59**	17.29	8.61
						2	15	**6.50**	**16.23**	**0.57**	**2.50**	7.07	18.73
						3	47-49	0.39	0.23	0.08	0.05	0.47	0.28
			0.45	3	Forage	1	21	3.04	2.70	0.34	0.34	3.38	3.04
						2	22	0.42	0.39	0.05	0.05	0.47	0.44
						3	61	0.07	0.05	0.02	(0.018)	0.09	0.07
					Hay	1	21	17.16	13.62	**1.59**	**1.37**	18.75	14.99
						2	22	1.99	1.70	**0.24**	**0.23**	2.23	1.93
						3	61	0.18	0.13	0.04	0.05	0.22	0.18
			0.30	4	Forage	1	14	3.41	3.77	**0.49**	**0.54**	3.9	4.31
						2	15	1.58	1.53	0.11	0.11	1.69	1.64
						3	54	0.10	0.10	0.02	0.02	0.12	0.12
					Hay	1	14	11.99	**13.84**	**2.73**	**1.99**	14.72	15.83
						2	15	7.25	6.67	**0.51**	**0.51**	7.76	7.18
						3	54	0.38	0.30	0.08	0.07	0.46	0.37
			0.30	5	Forage	1	21	2.72	2.66	**0.31**	**0.30**	3.03	2.96
						2	22	0.43	0.41	0.05	0.05	0.48	0.46
						3	61	0.04	0.03	(0.012)	(0.012)	0.06	0.05
					Hay	1	21	9.33	8.22	1.15	1.06	10.48	9.28
						2	22	2.85	2.67	0.26	0.21	3.11	2.88
						3	61	0.17	0.17	0.04	0.04	0.21	0.21
Freeborn, MN; 2007 RCN R070125	5	Viking 3000	0.46	2	Forage	1	14	**1.71**	**1.68**	0.12	0.13	1.83	1.81
						2	14	1.02	**0.81**	0.09	0.04	1.11	0.85
						3	47-48	**0.02**	**0.04**	**(0.007)**	**(0.010)**	0.04	0.06
					Hay	1	14	3.69	3.22	**0.55**	**0.48**	4.24	3.7
						2	14	4.00	3.71	0.32	0.31	4.32	4.02
						3	47-48	0.12	0.15	0.03	0.03	0.15	0.18
			0.45	3	Forage	1	21	0.69	0.69	0.10	0.10	0.79	0.79
						2	21	**0.62**	0.35	0.06	0.05	0.68	0.4
						3	50	**0.07**	0.05	**(0.016)**	(0.015)	0.09	0.07
					Hay	1	21	1.96	1.91	**0.31**	**0.32**	2.27	2.23
						2	21	1.20	1.44	**0.20**	**0.20**	1.4	1.64
						3	50	**0.40**	**0.30**	**0.11**	**0.09**	0.51	0.39
			0.30	4	Forage	1	14	**1.33**	**1.40**	0.17	0.19	1.5	1.59
						2	14	1.02	1.28	0.10	0.10	1.12	1.38

TABLE C.3. Residue Data from Alfalfa Field Trials with Pyraclostrobin (WDG).

Trial ID (City, State; Year)	Zone	Variety	Total Rate (lb ai/A)	Trt. [1] No.	Matrix	Cutting	PHI (days)	Residues (ppm) [2]					
								Pyraclostrobin		B 500-3		Combined [3]	
						3	43	**0.06**	**0.05**	(0.017)	(0.012)	0.08	0.07
					Hay	1	14	3.21	3.74	**0.51**	**0.53**	3.72	4.27
						2	14	2.95	2.91	**0.43**	0.23	3.38	3.14
						3	43	0.17	0.11	0.04	0.03	0.21	0.14
			0.30	5	Forage	1	21	0.75	**0.58**	0.10	0.09	0.85	0.67
						2	21	**0.61**	0.64	0.06	0.07	0.67	0.71
						3	50	**0.05**	**0.06**	(0.012)	(0.013)	0.07	0.08
					Hay	1	21	1.48	1.44	**0.24**	**0.25**	1.72	1.69
						2	21	1.74	1.93	**0.24**	**0.25**	1.98	2.18
						3	50	0.14	0.16	0.03	0.03	0.17	0.19
Stutsman, ND; 2007 RCN R070126	5	Mycogen 4A421	0.45	2	Forage	1	13	1.86	1.78	0.22	0.23	2.08	2.01
						2	12	2.60	2.30	0.35	0.33	2.95	2.63
						3	43-70	0.10	**0.14**	0.03	0.05	0.13	0.19
					Hay	1	13	3.05	5.22	**0.48**	**0.91**	3.53	6.13
						2	12	7.97	7.36	**1.32**	**1.22**	9.29	8.58
						3	43-70	**0.19**	**0.30**	0.05	**0.10**	0.24	0.4
			0.46	3	Forage	1	20	0.92	0.73	0.13	0.11	1.05	0.84
						2	20	1.80	1.84	0.20	0.21	2	2.05
						3	54	0.14	0.14	0.04	0.04	0.18	0.18
					Hay	1	20	2.88	2.98	**0.47**	**0.49**	3.35	3.47
						2	20	4.49	5.07	**0.60**	**0.66**	5.09	5.73
						3	54	**0.31**	**0.37**	**0.09**	**0.10**	0.4	0.47
			0.31	4	Forage	1	13	1.30	1.29	0.16	0.17	1.46	1.46
						2	12	3.08	3.32	0.34	0.35	3.42	3.67
						3	46	0.11	0.10	0.03	0.02	0.14	0.12
					Hay	1	14	6.31	7.14	**0.92**	**1.03**	7.23	8.17
						2	12	10.86	8.82	**1.61**	**1.34**	12.47	10.16
						3	46	**0.27**	**0.26**	0.06	0.06	0.33	0.32
			0.30	5	Forage	1	20	**0.43**	**0.44**	0.07	0.07	0.5	0.51
						2	20	1.13	1.21	0.13	0.16	1.26	1.37
						3	54	0.13	0.09	0.03	(0.020)	0.16	0.11
					Hay	1	20	1.90	2.10	**0.30**	**0.35**	2.2	2.45
						2	20	2.68	2.78	0.37	0.41	3.05	3.19
						3	54	**0.24**	**0.30**	0.05	**0.08**	0.29	0.38
Cache, UT; 2007 RCN R070127	9	355 Multileaf	0.47	2	Forage	1	12	3.33	3.87	**0.61**	**0.70**	3.94	4.57
						2	14	1.49	1.36	**0.24**	**0.20**	1.73	1.56
						3	43-54	0.15	0.20	0.03	0.04	0.18	0.24
					Hay	1	12	5.91	6.25	1.07	1.08	6.98	7.33
						2	14	5.58	6.06	0.93	1.00	6.51	7.06
						3	43-54	**0.54**	**0.56**	0.09	0.09	0.63	0.65
			0.46	3	Forage	1	19	0.80	0.85	**0.30**	**0.29**	1.1	1.14
						2	21	**0.47**	**0.44**	**0.13**	**0.11**	0.6	0.55
						3	55	0.10	0.08	0.02	0.02	0.12	0.1
					Hay	1	19	1.77	1.75	**0.59**	**0.54**	2.36	2.29
						2	21	1.86	1.68	**0.44**	**0.42**	2.3	2.1
						3	55	**0.47**	**0.37**	0.12	0.08	0.59	0.45

TABLE C.3. Residue Data from Alfalfa Field Trials with Pyraclostrobin (WDG).

Trial ID (City, State; Year)	Zone	Variety	Total Rate (lb ai/A)	Trt. [1] No.	Matrix	Cutting	PHI (days)	Residues (ppm) [2]					
								Pyraclostrobin		B 500-3		Combined [3]	
			0.30	4	Forage	1	12	3.98	**4.93**	**0.77**	**1.01**	4.75	5.94
						2	14	1.45	1.85	**0.26**	**0.34**	1.71	2.19
						3	48	0.15	0.15	0.03	0.03	0.18	0.18
					Hay	1	12	9.79	8.56	1.63	1.60	11.42	10.16
						2	14	7.05	6.57	**1.50**	**1.34**	8.55	7.91
						3	48	0.28	0.26	0.05	0.05	0.33	0.31
			0.31	5	Forage	1	19	**0.53**	**0.62**	0.18	0.18	0.71	0.8
						2	21	0.80	0.87	**0.16**	**0.17**	0.96	1.04
						3	55	0.16	0.16	0.04	0.04	0.2	0.2
					Hay	1	19	1.36	1.32	**0.43**	**0.40**	1.79	1.72
						2	21	2.61	2.60	**0.55**	**0.57**	3.16	3.17
						3	55	**0.42**	**0.36**	**0.14**	0.09	0.56	0.45
Stanislaus, CA; 2007 RCN R070128	10	Magna 5	0.45	2	Forage	1	13	1.53	1.55	0.23	0.20	1.76	1.75
						2	16	1.23	1.20	0.17	0.17	1.4	1.37
						3	46-48	0.03	0.03	(0.012)	(0.009)	0.05	0.05
					Hay	1	13	5.40	7.09	1.01	1.37	6.41	8.46
						2	16	5.32	**4.52**	**1.01**	**1.05**	6.33	5.57
						3	46-48	**0.68**	**0.16**	**0.19**	**0.04**	0.87	0.2
			0.45	3	Forage	1	22	**0.49**	**0.55**	0.12	0.13	0.61	0.68
						2	21	**0.31**	**0.26**	0.05	0.04	0.36	0.3
						3	49	0.02	(0.019)	(0.007)	(0.007)	0.04	0.04
					Hay	1	22	**3.24**	**2.61**	**0.94**	0.72	4.18	3.33
						2	21	1.20	1.13	0.23	0.18	1.43	1.31
						3	49	0.07	0.14	(0.019)	0.05	0.09	0.19
			0.30	4	Forage	1	13	**0.33**	**0.46**	0.07	0.09	0.4	0.55
						2	16	**0.51**	**0.48**	0.08	0.09	0.59	0.57
						3	44	(0.011)	(0.009)	(0.007)	(0.006)	0.04	0.04
					Hay	1	13	2.62	2.30	0.44	0.37	3.06	2.67
						2	16	2.41	2.54	0.36	0.44	2.77	2.98
						3	44	0.05	0.04	(0.015)	(0.014)	0.07	0.06
			0.30	5	Forage	1	22	**0.57**	**0.54**	0.12	0.13	0.69	0.67
						2	21	**0.27**	**0.19**	0.05	0.04	0.32	0.23
						3	49	(0.006)	(0.010)	(0.005)	(0.005)	0.04	0.04
					Hay	1	22	2.46	2.77	0.48	0.53	2.94	3.3
						2	21	1.59	1.28	0.22	0.19	1.81	1.47
						3	49	0.05	0.05	(0.017)	(0.015)	0.07	0.07
Power, ID; 2007 RCN R070129	11	355 Multi leaf	0.46	2	Forage	1	14	**0.50**	0.80	**0.07**	**0.09**	0.57	0.89
						2	14	1.29	1.19	**0.11**	**0.08**	1.4	1.27
						3	44-49	**0.13**	**0.11**	**0.03**	**0.02**	0.16	0.13
					Hay	1	14	2.39	2.86	0.31	0.31	2.7	3.17
						2	14	**4.46**	4.43	0.33	0.36	4.79	4.79
						3	44-49	**0.35**	**0.34**	0.06	0.05	0.41	0.39
			0.46	3	Forage	1	23	**0.04**	**0.04**	**(0.014)**	**(0.014)**	0.06	0.06
						2	22	1.01	1.12	**0.12**	**0.13**	1.13	1.25
						3	57	**0.09**	**0.09**	**0.03**	**0.03**	0.12	0.12
					Hay	1	23	**0.20**	**0.24**	0.05	0.05	0.25	0.29

TABLE C.3. Residue Data from Alfalfa Field Trials with Pyraclostrobin (WDG).

Trial ID (City, State; Year)	Zone	Variety	Total Rate (lb ai/A)	Trt. [1] No.	Matrix	Cutting	PHI (days)	Residues (ppm) [2]					
								Pyraclostrobin		B 500-3		Combined [3]	
						2	22	2.94	2.20	0.32	0.32	3.26	2.52
						3	57	0.10	0.09	0.02	(0.015)	0.12	0.11
			0.30	4	Forage	1	14	0.76	0.75	**0.07**	**0.07**	0.83	0.82
						2	14	1.10	1.42	**0.09**	**0.10**	1.19	1.52
						3	49	**0.11**	**0.11**	**0.03**	**0.03**	0.14	0.14
					Hay	1	14	3.88	3.25	0.23	0.21	4.11	3.46
						2	14	4.61	4.29	0.28	0.26	4.89	4.55
						3	49	0.25	0.24	0.05	0.04	0.3	0.28
			0.30	5	Forage	1	23	**0.04**	**0.05**	**(0.013)**	**(0.013)**	0.06	0.07
						2	22	0.80	0.89	**0.13**	**0.13**	0.93	1.02
						3	57	**0.11**	**0.10**	**0.03**	**0.03**	0.14	0.13
					Hay	1	23	0.16	**0.26**	0.04	0.05	0.2	0.31
						2	22	3.05	2.32	0.39	0.30	3.44	2.62
						3	57	0.42	0.40	0.09	0.09	0.51	0.49

[1] Treatments #2 and #3 included three pyraclostrobin applications at ~0.144 lb ai/A/application with the first and second applications made prior to the 1st cutting and the final application made prior to the 2nd cutting. Treatments #4 and #5 included two applications at ~0.144 lb ai/A/application, with the first application made prior to the 1st cutting and the second application made prior to the 2nd cutting.

[2] Residues are reported in parent equivalents. The LOQ is 0.02 ppm for each analyte, for a combined LOQ of 0.04 ppm; the LOD is 0.004 ppm for each analyte. The values <LOQ and >LOD are reported in parentheses.

[3] For calculating combined residues, the LOQ was used for any values reported as <LOQ.

[4] The average of multiple analyses is reported in **bold**.

NR= not reported.

TABLE C.4. Summary of Combined Residue Data from Alfalfa Field Trials with Pyraclostrobin (WDG).

Commodity	Total Applic. Rate (lb ai/A)	Trt. No.[1]	Cutting	PHI (days)	Combined Residue Levels (ppm)[2]						
					n	Min.	Max.	HAFT[3]	Median	Mean	Std. Dev.
Alfalfa Forage	0.44-0.47	2	1st	12-15	24	0.44	7.24	6.69	2.07	2.99	2.02
			2nd	12-16	24	0.85	8.15	7.41	1.55	2.69	1.97
			3rd	43-73	22	<0.04	0.24	0.21	0.07	0.09	0.06
	0.45-0.47	3	1st	19-23	24	0.06	3.38	3.21	0.79	0.89	0.81
			2nd	20-23	24	0.30	2.59	2.47	0.97	1.15	0.72
			3rd	49-76	22	<0.04	0.18	0.18	0.06	0.08	0.04
	0.29-0.31	4	1st	12-15	24	0.40	5.94	5.35	1.91	2.31	1.56
			2nd	12-16	24	0.57	6.56	6.42	1.97	2.65	1.77
			3rd	43-70	22	<0.04	0.18	0.18	0.05	0.08	0.05
	0.30-0.31	5	1st	19-23	24	<0.04	3.03	3.00	0.67	0.80	0.79
			2nd	20-23	24	0.23	2.87	2.78	1.03	1.12	0.63
			3rd	49-76	22	<0.04	0.20	0.20	0.05	0.08	0.05
Alfalfa Hay	0.44-0.47	2	1st	12-15	24	1.42	20.49	19.77	6.60	7.84	5.27
			2nd	12-16	24	4.02	22.87	22.19	7.07	9.28	5.47
			3rd	43-73	22	0.05	0.87	0.64	0.22	0.27	0.23

TABLE C.4. Summary of Combined Residue Data from Alfalfa Field Trials with Pyraclostrobin (WDG).

Commodity	Total Applic. Rate (lb ai/A)	Trt. No.[1]	Cutting	PHI (days)	Combined Residue Levels (ppm)[2]						
					n	Min.	Max.	HAFT[3]	Median	Mean	Std. Dev.
	0.45-0.47	3	1st	19-23	24	0.08	18.75	16.87	2.27	3.44	4.45
			2nd	20-23	24	1.31	8.01	7.72	3.56	3.57	1.89
			3rd	49-76	22	<0.04	0.59	0.52	0.15	0.20	0.18
	0.29-0.31	4	1st	12-15	24	1.28	15.83	15.28	6.37	7.44	4.44
			2nd	12-16	24	2.77	18.81	17.93	7.86	8.59	4.51
			3rd	43-70	22	0.05	0.46	0.42	0.12	0.18	0.13
	0.30-0.31	5	1st	19-23	24	0.20	10.48	9.88	1.72	2.61	2.80
			2nd	20-23	24	1.47	12.21	10.70	3.18	3.90	2.34
			3rd	49-76	22	<0.04	0.56	0.51	0.13	0.20	0.17

[1] Treatments #2 and #3 included three pyraclostrobin applications at ~0.14 lb ai/A/application with the first and second applications made prior to the 1st cutting and the final application made prior to the 2nd cutting. Treatments #4 and #5 included two applications at ~0.14 lb ai/A/application, with the first application made prior to the 1st cutting and the second application made prior to the 2nd cutting.

[2] The combined LOQ for residues of pyraclostrobin and BF 500-3 is 0.04 ppm. For purposes of calculating median and mean and standard deviation, the LOQ (0.04 ppm) was used for residue values <LOQ.

[3] HAFT = Highest Average Field Trial.

D. CONCLUSION

The submitted alfalfa field trial data are adequate and would support the use of two or three broadcast foliar applications of pyraclostrobin (WDG) to alfalfa at up to ~0.15 lb ai/A/application, with no more than two applications per cutting, for maximum seasonal use rates 0.30 or 0.45 lb ai/A. The data also support a minimum RTI of 14 days and minimum PHIs of either 14 or 21 days.

E. REFERENCES

DP#s: 269668, 272771, 272789, 274095, 274192, 274471, 274957, 275843, and 278429
Subject: PP#0F06139. Pyraclostrobin on Various Crops: Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits, Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean), Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits, Strawberry, Sugar Beet, Tree Nuts, Tuberous and Corm Vegetables, and Wheat. Review of Analytical Methods and Residue Data. EPA File Symbols:
From: L. Cheng
To: C. Giles-Parker/J. Bazuin
Dated: 11/28/2001
MRIDs: 45118428-451184-37, 45118501-45118512, 45118514-45118537, 45118601-45118625, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and 45429901

DP Barcode: D269850
Subject: PP# 0F06139. Pyraclostrobin (BAS 500F) in or on Various Crops. Request for Tolerance Method Validation (TMV) Trial.
From: L. Cheng
To: F. D. Griffith, Jr.
Dated: 11/8/2000
MRIDs: 45118505, 45118504, 45118509, 45118510, 45118501, 45118503, 45118507, 45118514

F. DOCUMENT TRACKING

RDI: W. Cutchin (9/18/09)
Petition Number: 9F7528
DP #: 367409
PC Code: 099100

Template Version June 2005

13544

R179117

Chemical Name: Dinotefuran

PC Code: 044312
HED File Code: 51100 RD Chemistry Reviews
Memo Date: 11/17/2009
File ID: 00000000
Accession #: 000-00-0132

HED Records Reference Center
11/19/2009